SYNTHESIS AND SWITCHABILITY STUDY OF AMIDINE-CONTAINING VINYL MONOMERS AND THEIR POLYMERS

SYNTHESIS AND SWITCHABILITY STUDY OF AMIDINE-CONTAINING VINYL MONOMERS AND THEIR POLYMERS

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ABSTRACT

As a type of inexpensive and non-invasive stimuli for switchable materials, CO_2 has been used to trigger the property changes of switchable gels, solvents, surfactants and solutes. These materials have applications in art work cleaning, organic reactions, plastic recycling and redispersible latex and so on.

In this thesis work, two new CO_2-responsive monomers have been synthesized. These amidine-containing monomers were prepared in a simple and effective one-step reaction, giving a very high yield (98.5 %) of product. Furthermore, there was no complicated further purification required to obtain the highly pure product. The CO_2 switchability, conductivity and partitioning of the monomers were measured. It was confirmed that the monomers could be protonated CO_2 in the present of trace amount of water and reversibly switched back and forth to their natural forms by N_2 at room temperature.

The polymers having different molecular weights were prepared from one monomer via conventional free radical polymerization method. The polymers also showed the reversible switchability property with CO_2 and N_2 stimuli. This was confirmed by the results of conductivity and partitioning tests. Temperature showed a major influence on the conductivity of the monomer and polymers. The effect of molecular weight on the polymer switchability of was further investigated through conductivity tests and potentiometric titration. The conductivity decreased with the increased molecular weight. The apparent equilibrium constant (pK_a) decreased with the degree of protonation (δ) suggesting that the basicity of the polymers is strongly depended on the value of δ.

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INTRODUCTION

1.1. Switchable Materials

Switchable materials are the ones that possess multiple characteristics and/or properties and can be switched reversibly between the different properties via stimuli from their environment and their properties can be changed dramatically by external stimuli. Switchable materials can be employed in many applications including information technology, controlled uptake and release, optical memory, smart glass, analytical devices and so on (Lampert 2004). Some fascinating applications of switchable materials including inorganic, organic and polymeric materials are introduced in the following sections of this chapter.

1.1.1. Inorganic Materials

Many inorganic switchable materials have exceptional photo, magnetic and electrical properties (Lampert 2004). Chromogenics is known as smart materials, which cover a wide range of uses in glazing, mirrors, privacy windows and transparent electronic displays (Lampert 2004). Commonly used chromogenics include electrically powered, photochromic and thermochromic materials. The use of chromogenics started from 1704, which was the discovery of the chemical coloration of Prussian Blue. Then, electrochemical coloration was found in bulk tungsten oxide in the 1930s, and electrochemical coloration was found in thin films in the 1950s. In 1969, electrochromic devices were made in the first time. Later, the devices were used for displays, automobiles and glazing applications (Lampert 2004). Typically, coloration ions like H^+, Li^+ and Ag^+ are used for electrochromic glazing. The Li^+ intercalation of reaction for a cathodic coloring material is:

$$\mathrm{WO_3 + y\,Li^+ + y\,e^- \leftrightarrow Li_yWO_3}$$

(colourless) (blue)

A complementary anodic nickel vanadium oxide reaction is:

$$\mathrm{Li_yNi_zV_{2-z}O_5 - y\,Li^+ - y\,e^- \leftrightarrow Ni_zV_{2-z}O_5}\P$$

(light gray) (colourless)

When a low voltage is applied, the electrochromic glass can change color reversibly from colorless to other color with lower transparency. This technology has been designed for building windows, roof and visors on motorcycle helmets (Lampert 2004). Thermotropics materials exhibit a clear appearance at lower temperature, but appear opaque at higher temperature, which can be used for skylights, glazing and upper windows (Lampert 2004).

Titanium dioxide (TiO_2) is a type of very important inorganic material that has been used in applications including photo-splitting of water, photocatalysis and photovoltaic devices (Fujishima 1972, O'Regan 1991, Linsebigler 1995). Jiang and co-workers (Feng 2005) developed a type of TiO_2 based superhydrophilicity/ superhydrophobicity switchable materials with a mechanism of cooperation of the hierarchical microstructures, the orientation of crystal planes and surface photosensitivity. TiO_2 nanorod films were deposited on glass substrates to give the surface superhydrophilicity. When the glass substrates were exposed under UV light, the wettability changed to superhydrophobic. When the substrates were stored in darkness, the surfaces were reversibly switched back to superhydrophilic again. The SEM pictures of the TiO_2 nanorod film and the switchable surface tension test results are shown in Figure 1.1 (Feng 2005).

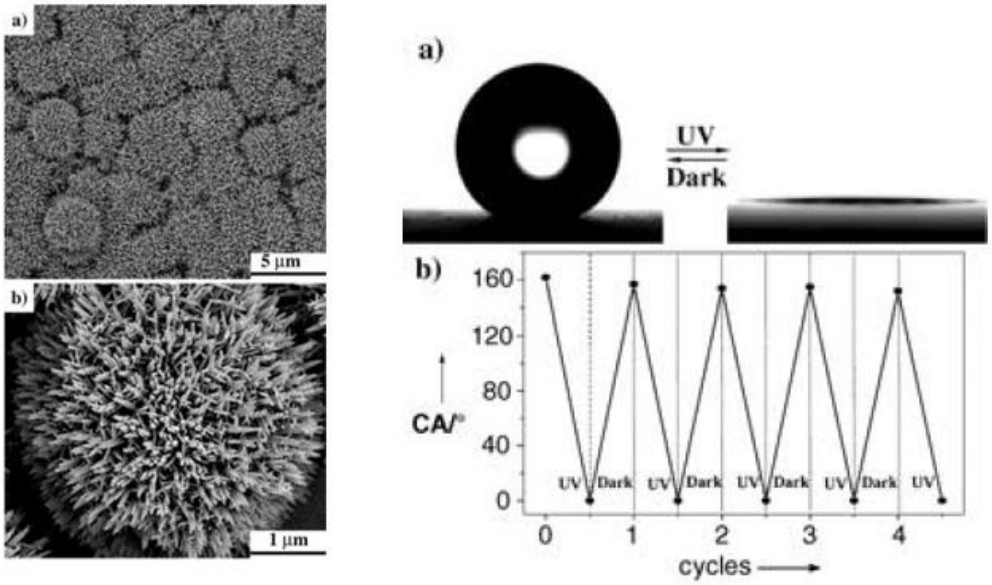


Figure 1.1: Low-magnification FE-SEM image of a TiO_2 nanorod film deposited on a glass wafer (left a); morphology of a single papilla at high magnification (left b); photographs of a spherical water droplet with CA of (154 ± 1.3) ° and a flat water film with CA of 0 ° before and after the films were exposed to UV illumination, respectively (right a) and the reversible superhydrohobicity/superhydrophobicity transition of the as-prepared films by alternating UV irradiation and storage in the dark (right b) (Feng 2005)

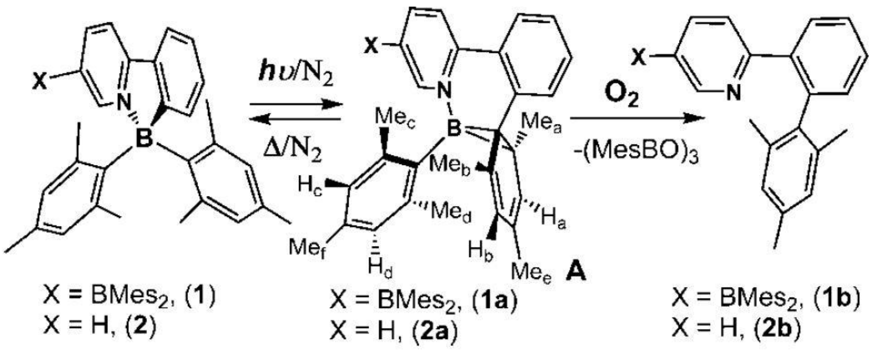
In the development of switchable optical memory, $Ge_2Sb_2Te_5$ or GST composition can be repeatedly switched between crystalline and amorphous states by light or electrical pulse with appropriate intensities and durations (Baker 2006). Many magnetic switchable inorganics, especially transition metal compounds, have been well studied. The magnetic materials with bistability and hysteresis loops have drawn lots of attention due to their potential applications in molecular switches and memory (Sato 2007). Photoirradiation, electrochemical redox reactions, uptake and release of ions and guest molecules, and external pressures can be the triggers of magnetic property changes (Sato 2007). The study of switchable magnetic materials is attracting more and more attention from researchers. Besides the examples mentioned above, numerous investigations on switchable inorganic with various properties and structures have been reported.

1.1.2. Organic Materials

Many organic materials are found to possess switchable properties. The oldest form of synthetic molecules can be used as switches are the pH indicators which are halochromic chemical compounds displaying different color in solutions with different pH.

Similar to inorganic materials, organic or inorganic-organic complex switchable materials can respond to many types of external stimuli with changes in various properties. The applications of organic switchable materials include active photonic bandgap materials, second-order non-linear optical materials and reversible optical data storage and so on (Gaudry 2000, Feringa 1993, Jakubiak 2003).

Organoboron compounds with a conjugate chromophore have been extensively studied in the past decade for applications in optoelectronic materials and devices. Because they are highly thermal and chemical stable, the four-coordinate organoboron compounds became the ideal candidates for organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic thin film transistors (OTFTs) materials. Wang and co-workers (Rao 2008, Baik 2009, Amarne 2010) developed a new type of diboron molecules which will undergo a reversible isomerization process involving a tetrahedral boron center and the formation/breaking of a C-C bond. In this process, these compounds will also display reversible photo-thermal color switching under exposure of UV light and heat under the protection of N_2. However, the decomposing of these compounds in the presence of O_2 will limit their application.



Scheme 1.1: Transformation of a diboron molecule (5-$BMes_2$-2-ph-py)$BMes_2$ (Rao 2008)

Recently, two research groups (Pal 2010, Lekin 2010) reported two organic materials with bistability and paramagnetic property. The organic radicals undergo a monomer-dimer transition with change in temperature also demonstrate a paramegnetic/

diamagnetic process. A hysteresis phenomenon was found during the temperature controlled monomer/dimer switching process (shown in Figure 1.2).

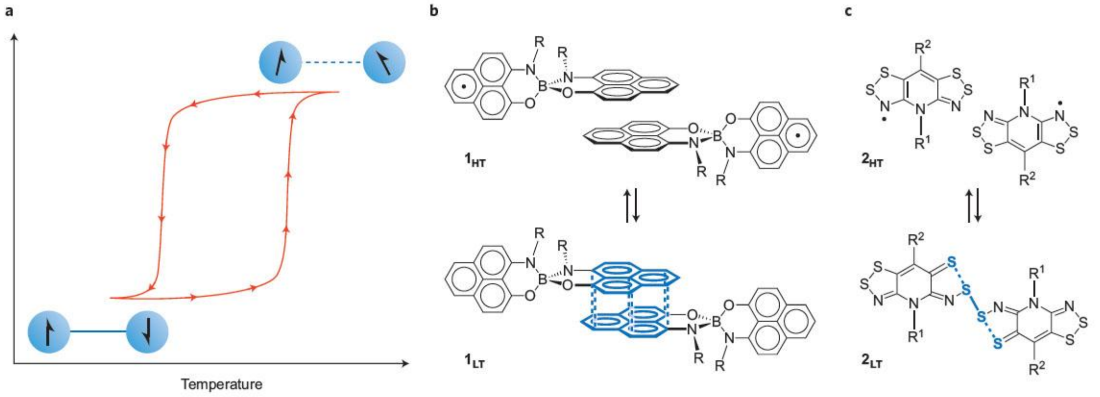


Figure 1.2: Schematic diagram of thermal hysteresis arising from a transition between monomeric organic radicals at high temperature and diamagnetic dimers at low temperatures (a) and high-temperature (HT) form and low temperature form (LT) of the radicals (b) (Pal 2010, Lekin 2010)

The tetrathiafulvalene (TTF) unit and its derivatives have attracted more attention due to their new-found properties: a high π-donating ability and occurrence of three stable redox states. Many types TTF-based molecular structures have been designed and used in the application of molecular sensors, redox fluorescent switches, electrochemically-driven conformational controls, molecular clips and tweezers and redox-controlled gelation processes (Canevet 2009).

1.1.3. Polymeric Materials

An essential process for living systems to sustain life and maintain biological function is the response to stimuli of their environment. To adapt to changes, living systems usually tailor their molecular assemblies and interfaces to provide specific chemical functions and structures. By learning from nature, researchers have been designing various stimuli-responsive polymers (Jeong 2002). Similarly to the natural occurring macromolecules, these synthetic polymers can respond to one or multiple subtle changes in their surrounding environment, and adapt to them with changes in physiochemical property changes, often in a dramatic manner (Jeong 2002, Stuart 2010). These switchable properties include shapes, surface characteristics, solubility, formations of an intricate molecular self-assembly, sol-to-gel transition and etc. Sometimes, these properties of stimuli-responsive polymers could be reversibly triggered by certain types of "switch" according to their chemical structures. Smart polymeric materials are very useful and have been well studied for many applications. In the following part of this chapter, some stimuli-responsive polymers and complexes of polymers and switchable small molecules that have high potentials for applications; especially the ones that their properties could be reversibly switched of their properties will be introduced.

1.2. Stimuli Responsive Polymers

Stimuli responsive polymers have different physical forms including free chains in solutions and nanostructured polymer systems which are shown in Figure 1.3 (Stuart 2010). These structures mainly include macromolecular assemblies in thin films such as polymer brushes, multilayered films formed by different polymers, hybrid systems that combine polymers and particles, thin film of polymer networks and membrane with channels or pores; and nanoparticles such as micelles, nanogels, capsules and vesicles, core-shell particles, hybrid particle-in-particle structures and their assemblies in solutions and at interfaces of emulsions and foams.

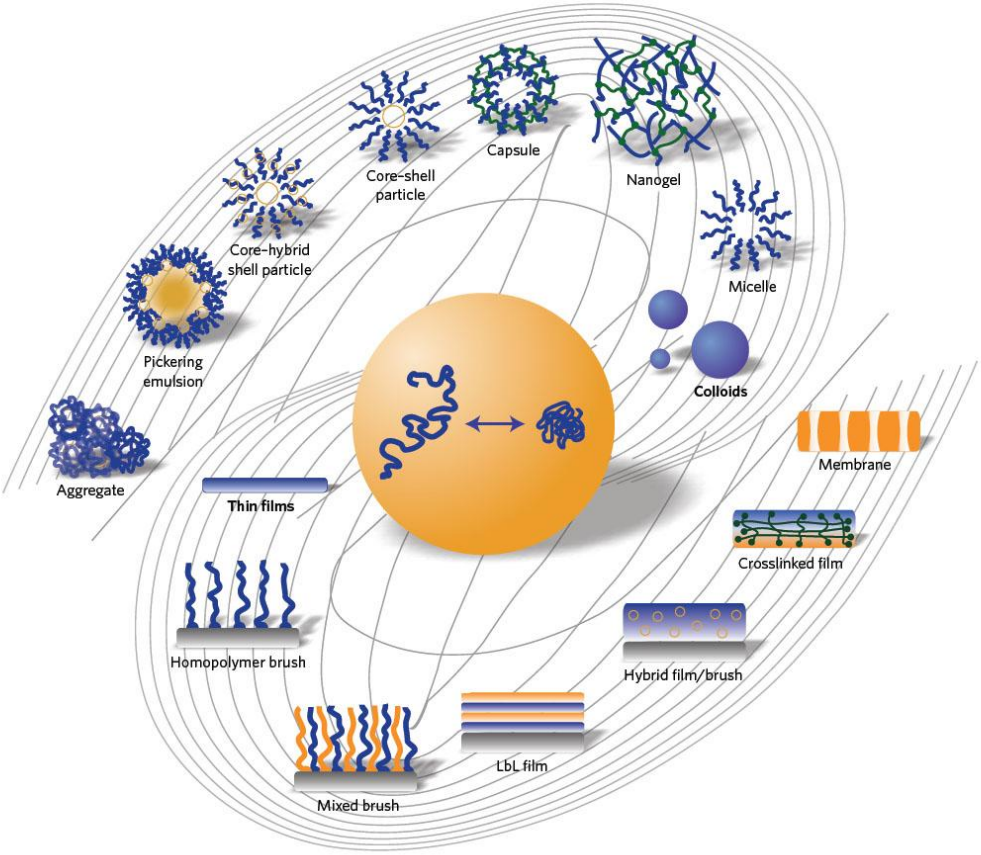
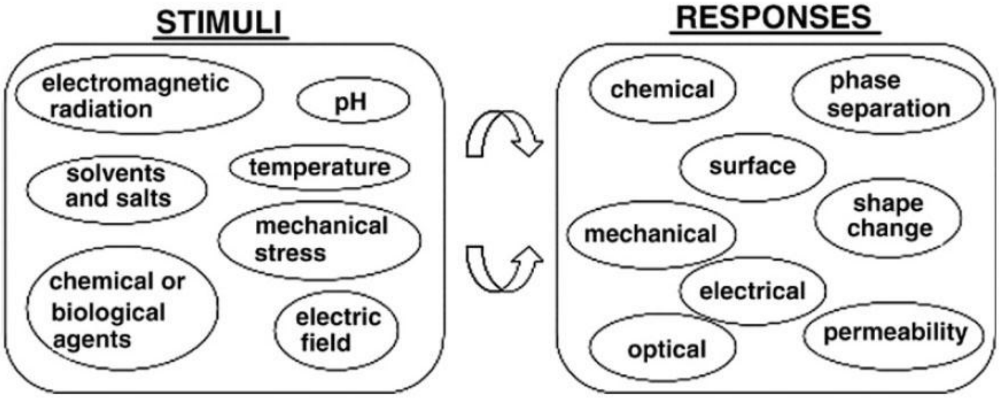


Figure 1.3: "Galaxy" of nanostructured stimuli-responsive polymer materials (Stuart 2010)

Environmental stimuli could be the temperature (Tanaka 1978, Hirokawa 1984, Amiya 1987, Chen 1995, Schmaljohann 2006), pH (Schmaljohann 2006), light (Irie 1993, Suzuki 1990), ionic strength (Tanaka 1980), chemicals (Mendes 2008, Roy 2010), electric fields (Tanaka 1982, Osada 1992) and magnetic fields (Szabo 1998) (Scheme 1.2). The development of many types of functional stimuli-responsive polymers and their various nanostructures enabled several novel applications in controlled drug delivery and release systems (Jhaveri 2009, Hoffman 2008, Bayer 2008) tissue engineering (Leclerc 2004), bioseparation (Nagase 2008), diagnostics (Kippelen 1998), responsive biointerfaces (Senaratne 2005, Ionov 2009), coatings with interaction with and response to the environment (Mendes 2008, Roy 2010, Luzinov 2008, Motornov 2003), sensors (Anker 2008, Tokarev 2009), actuator (Liu 2000) and so on.



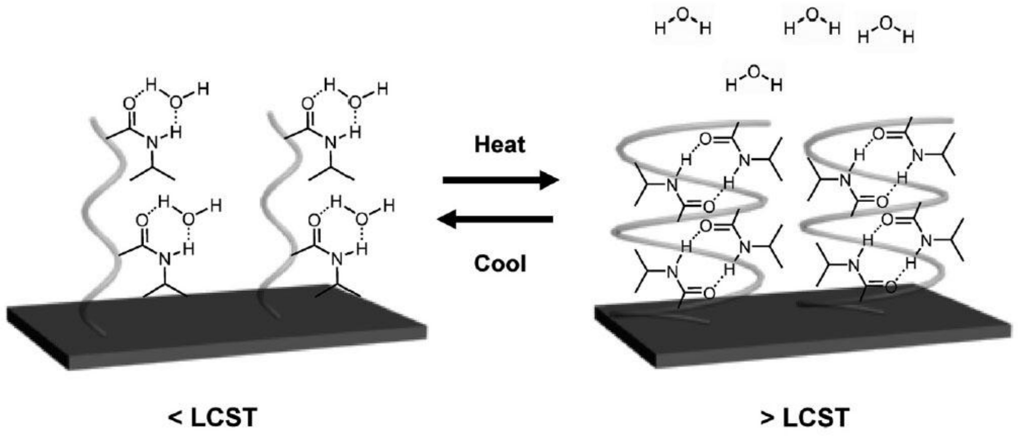
Scheme 1.2: Potential stimuli and responses of synthetic polymers (Schmaljohann 2006)

Most of the applications of stimuli-responsive synthetic polymers are based on the structures they can form as mentioned above and displayed in Figure 1.3.

1.2.1. Temperature Responsive Polymers

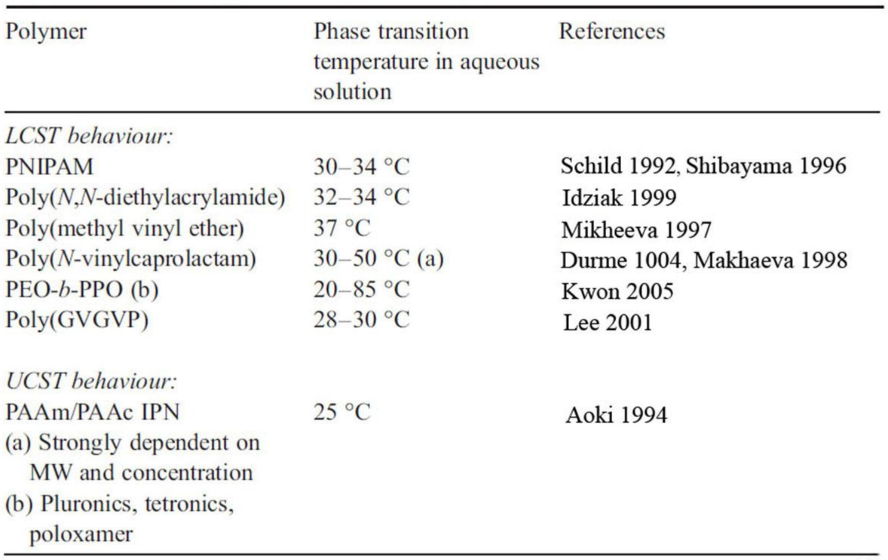
Temperature stimulation is a convenient and widely used method to control the properties of polymer nanostructures. Many themo-responsive polymers with different responsive temperatures especially those polymers with responsive temperatures in the physiological region have been developed and studied (Heskins 1968, Pelton 1986, Hirokawa 1999).

A type of very important thermo-responsive polymer, which has drawn the greatest attention so far is poly(N-isopropylacrylamide) (PNIPAM) and its copolymers. It has been widely studied since the first report by Guillet and co-workers (Heskins 1968). PNIPAM has a phase transition temperature referred to as a lower critical solution temperature (LCST) of 32 °C in aqueous solution. At a lower temperature of LCST, PNIPAM polymer chains will form intermolecular hydrogen bonds with water molecules, which yield an extended, solvent-swelled conformation (Scheme 1.3 left). While above LCST, PNIPAM polymer chains will form intramolecular hydrogen bonds between C=O and N-H groups as a collapsed morphology that excludes solvent (Scheme 1.3 right) (Mendes 2008, Roy 2010). In a study (Hirokawa 1999) involving laser scanning confocal microscopy (LSCM), a continuous two-domain internal structure with dense and sparse regions was found in PNIPAM gel.



Scheme 1.3: Diagram illustrating the temperature-induced switching of a PNIPAM-modified surface (Mendes 2008)

Table 1.1: Selected polymers with LCST and UCST behavior in the temperature region interesting for biomedical applications (Schmaljohann 2006)



Polymer	Phase transition temperature in aqueous solution	References
LCST behaviour:		
PNIPAM	30–34 °C	Schild 1992, Shibayama 1996
Poly(*N*,*N*-diethylacrylamide)	32–34 °C	Idziak 1999
Poly(methyl vinyl ether)	37 °C	Mikheeva 1997
Poly(*N*-vinylcaprolactam)	30–50 °C (a)	Durme 1004, Makhaeva 1998
PEO-*b*-PPO (b)	20–85 °C	Kwon 2005
Poly(GVGVP)	28–30 °C	Lee 2001
UCST behaviour:		
PAAm/PAAc IPN	25 °C	Aoki 1994
(a) Strongly dependent on MW and concentration		
(b) Pluronics, tetronics, poloxamer		

An important reason for the application of PNIPAM in biology is that it undergoes a sharp property change in response to a moderate and near physiological temperature stimulus (Mendes 2008, Roy 2010). The PNIPAM grafted surface exhibits the different cell adhesion behaviors below and above the LCST during the reversible volume phase transition of PNIPAM (Yamada 1990).

There are also some polymers that behave differently as PNIPAM: they become soluble upon heating and become insoluble at lower temperature. This phase transition temperature is called the upper critical solution temperature (UCST) (Schmaljohann 2006, Mendes 2008, Roy 2010). Only the aqueous systems of LCST and UCST polymers are of interest for biomedical applications and are widely studied, though other non-aqueous ones also exist (Schmaljohann 2006). Among the water soluble systems, typical LCST polymers are polymerized from monomers including N-isopropylacrylamide (NIPAM)

(Schild 1992, Shibayama 1996), N, N-diethylacrylamide (DEAM) (Idziak 1999), methylninylether (MVE) (Horne 1971), and N-vinylcaprolactam (NVCl) (Van Durme 2004); a typical UCST system is based on a combination of acrylamide (AAm) and acrylic acid (AAc) (Aoki 1994). The transition temperatures in aqueous solutions of these polymers are listed in Table 1.1 (Schmaljohann 2006).

Poly(N, N-diethylacrylamide) (PDEAM) has a transition temperature similar to PNIPAM. The thermo-responsive property of PDEAM, however, is strongly affected by the tacticity of the polymer (Schild 1992, Shibayama 1996). On the other hand, the biocompatibility and independency of its transition temperature to molecular weight and concentration make PNIPAM the most prominent candidate in biomedical applications such as controlled release systems. Furthermore, the LCST of PNIPAM based copolymer can be adjusted by copolymerization of a second monomer to change the apparent hydrophilic/hydrophobic composition. For example, the microgel comprising of NIPAM and maleic acid (MA) with a ratio of 9/1 was found to have a volume phase-transition temperature (VPTT) in a desired narrow range of 38 to 41 °C at pH = 7.4 in phosphate-buffered saline (PBS). At 37 °C, there is no notable volume change of the microgels, while the size of microgels decreases almost 8-fold with temperature increased to 41 °C (Das 2007). The volume change is reversible.

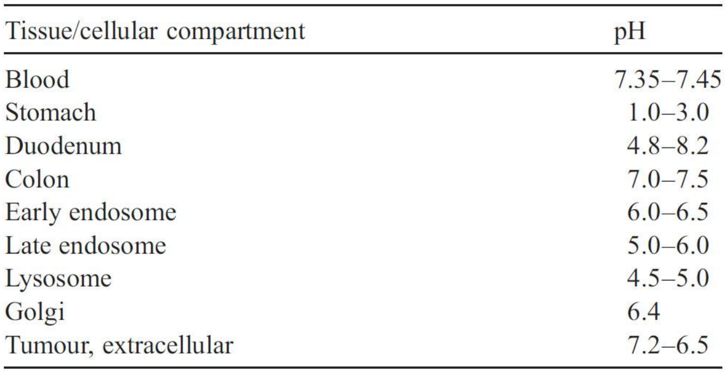
Besides poly(N-alkylacrylamide)s, some other polymers and copolymers were found to be temperature sensitive and of interest for biomedical applications (Schild 1992). Poly(methyl vinyl ether) (PMVE) exhibits a transition temperature of exactly

37 °C and typical type III demixing behavior (Moerkerke 1998). Poly(N-vinyl caprolactam) (PVCa) possesses a transition temperature of 33 °C and other interesting properties such as biocompatibility, high absorption ability and solubility in both water and organic solvents (Makhaeva 1998). Polypeptides with a good balance of hydrophilic and hydrophobic residues also possess LCST behavior (Urry 1997). The copolymer brushes with different composition and different side chain lengths of three comonomers, 2-(2-methoxyethoxy) ethyl methacrylate (MEO_2MA), hydroxyl-terminated oligo (ethylene glycol) methacrylate (HOEGMA) and 2-hydroxyethyl methacrylate (HEMA), have their collapse transition temperature between 20 to 40 °C (Laloyaux 2010).

1.2.2. pH-Responsive Polymers

Another type of well-studied important materials in biomedical applications is the pH-responsive polymers, whose solubility, configuration, conformation and volume can be reversibly changed by external pH stimulus (Park 1997, Roy 2003). pH-Responsive polymer systems have potential uses as "smart" functional materials, if their properties could be tailored and manipulated according to the physiological pH condition (Table 1.2) (Grabe 2001, Watson 2005). For example, because the extracellular pH of tumour is 6.5-7.2, the release of anti-cancer drug from a designed drug delivery and release system could be triggered by the pH decrease in vivo. The controlled drug delivery and release system would maximize the drug efficiency and minimize the damage to health tissues (Dai 2008).

Table 1.2: pH In various tissues and cellular compartments (Dai 2008)



Tissue/cellular compartment	pH
Blood	7.35–7.45
Stomach	1.0–3.0
Duodenum	4.8–8.2
Colon	7.0–7.5
Early endosome	6.0–6.5
Late endosome	5.0–6.0
Lysosome	4.5–5.0
Golgi	6.4
Tumour, extracellular	7.2–6.5

Some commonly studied pH-responsive polymer materials include homopolymers and copolymers of poly(N, N-dimethylaminoethyl methacrylate) (PDMAEMA), poly(N, N-diethylaminoethyl methacrylate) (PDEA), polyacrylic acid (PAA), polymethacrylic acid (PMAA) and poly(L-lysine) (PLL). PDMAEMA is both thermo- and pH-responsive (Dai 2008).

The behavior of block copolymers of PDMAEMA and poly(methyl methacrylate) (PMMA) has been studied by Armes and co-workers (Baines 1996). After the nearly quantitative quaternization of the PDMAEMA blocks of the copolymer, its water-solubility was enhanced, and micelles were formed at a wide range of pH. At an acidic pH, the PDMAEMA blocks are water soluble because of the protonation. While at a neutral or basic pH, the PDMAEMA blocks are also water soluble due to the hydrogen bonding between polymer chains and water molecules. It is observed that at a pH of 9.5, the size of micelles formed by PDMAEMA-b-PMMA increased with the addition of the electrolyte and finally macroscopic precipitation was observed with the further addition of the electrolyte. The LCST of PDMAEMA is in a range of 32-52 °C depending on its molecular weight at neutral or basic pH. For block copolymer of polystyrene (PS) and PDMAEMA brushes grafted on silica surfaces, in different solvents they form different conformations due to their different solubilities of two blocks. Dry films formed by this type of copolymers show different hydrophilic characteristics depending on solvent treatments (Zhao 2000).

Compared to PDMAEMA, PDEA is more hydrophobic and only pH-responsive but not thermo-responsive (Dai 2008). The diblock copolymer of poly(ethylene oxide) (PEO) and PDEA exhibited on pH-dependence (Zhong 2005). PEO-b-PDEA formed micelles with a hydrodynamic radius of about 19 nm at high pH when the PDEA blocks are ionized. While, at a lower pH, the two blocks became both water-soluble and the polymer chains exhibited the hydrodynamic radii of about 6-7 nm as unimers. The copolymer has the potential of applications in the target release of drugs in the tumor or other lower pH sites.

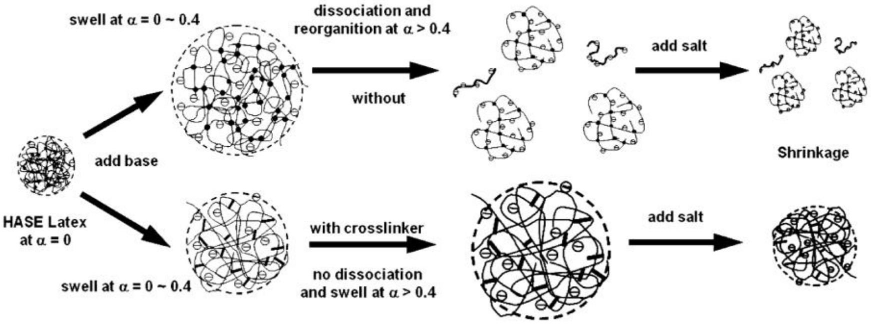


Figure 1.4: The mechanism of self-assembled microgels for HASE with increasing pH and salt concentration (Brazel 1995)

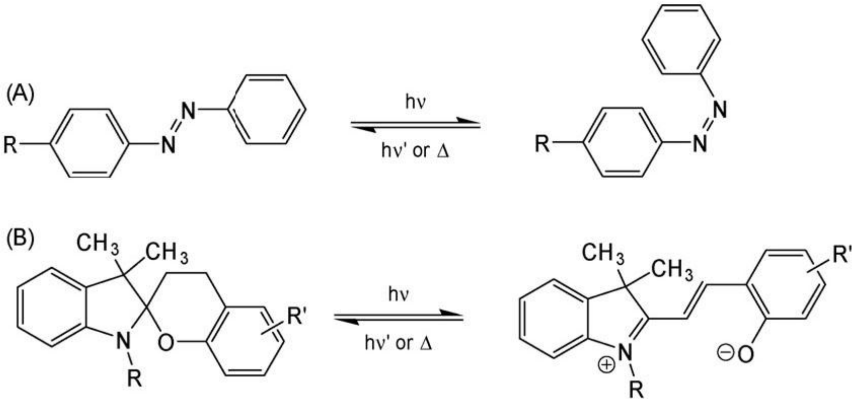
Hydrogels comprising MAA and NIPAM exhibit both thermo- and pH-responsive behaviors (Brazel 1995). The mesh size of these hydrogels changes dramatically between collapsed and swollen states depending on the change of pH. This system is promising for applications in size-selective permeation or controlled drug delivery and release system. The LCST of this hydrogel system increases with an increasing composition of the MAA component. The hydrophobically modified alkali-soluble emulsions (HASE) comprising with MAA, ethyl acrylate (EA) and a macromonomer ended with a hydrophobic group (Guo 1998) are affected by chain composition, pH, temperature, salt and surfactant (Figure 1.4) (Wang 2000, Dai 2000, Dai 2001, Dai 2002, Dai 2003, Dai 2005).

1.2.3. Photo-Responsive Polymers

Since irradiation as a stimulus is straight-forward and non-invasive in inducing responsive behavior, the research of photo-responsive polymers has expanded recently (Roy 2010). Irradiated photo-responsive polymers with light of an appropriate wavelength can change their properties (Kumar 1989, Dai 2009), making this type of polymers could be potentially useful in such applications as drug delivery (Nagasaki 2008), non-adhesive surfaces (Higuchi 2004, Edahiro 2005), biomedical imaging (Kippelen 1998), reversible optical storage (Ruhmann 1997, Lee 2006), polymer viscosity control (Moniruzzaman 2007), photomechanical transduction and actuation (Natansohn 2002) and tissue engineering (Leclerc 2004).

Polymers containing azobenzene and spiropyran moieties are the most widely studied photo-responsive polymeric materials (Kumar 1989, Dai 2009, Moniruzzaman

2007, Yager 2006, Zhao 2009, Jochum 2009, Such 2004, Lee 2006, Ivanov 2002, Konak 1997, Lee 2007). The property changes of electronic structure, geometric shape and polarity of the derivatives of azobenzene- and spiropyran- containing materials are shown in Scheme 1.4 (Roy 2010, Natansohn 2002, Allnso 2001, alonso 2000, Matejka 1981).



Scheme 1.4: Reversible photo-induced transformations of (a) azobenzene and spiropyran derivatives (Roy 2010)

The *trans*-form azobenzene group is more stable and with no dipole moment, while the *cis*-form is very polar and has a dipole moment (Roy 2010, Kumar 1989, Dai 2009). These two forms can be switched reversibly by irradiation (Scheme 1.4 a) (Mendes 2008). Thus, the azobenzene-containing polymers with variable shapes, self-assembly behaviours and polarity can be obtained under exposure of light with certain wavelength (Viswanathan 1999). Wang and co-workers (Deng 2007, Li 2005) reported a type of azobenzene-containing epoxy-based polymer colloids with a photo-induced deformation. The morphology of the colloids could be changed from sphere to spindles and rods according to the different wavelength of irradiation. An azobenzene group incorporated methylcellulose complex has the phototunable sol-gel transition property

(Arai 1995). Incorporation of azo chromophores into the other types of stimuli-responsive polymers, such as PNIPAM, PDMAEMA and PAA, enables new functions of multiple stimuli-responsive systems (Lee 2006, Khoukh 2007, Li 2006, Desponds 2003). Azobenzene groups can also be used to photo-switch supramolecular assembly behavior, furthermore to change the properties of bulk materials, surfaces and polymeric aggregates in solution by irradiation (Natansohn 2002, Yager 2006, Delair 2000, Yager 2001).

A spiropyran group is relatively non-polar, but after irradiation of light with an appropriate wavelength, it transforms to a zwitterionic merocyanine isomer with a larger dipole moment. This polarity switching process can also be reversed by irradiation of visible light as shown in Scheme 1.4 b (Roy 2010). Matyjaszewski and co-workers (Lee 2007) prepared a type of photo-responsive polymeric micelles by using a spiropyran containing methacrylate monomer and PEO. The micelles formed in aqueous solution can be dissociated by UV irradiation and regenerated upon irradiation with visible light. The dye used in the experiment could be released through the control of micelles via UV irradiation and re-encapsulated by visible light irradiation.

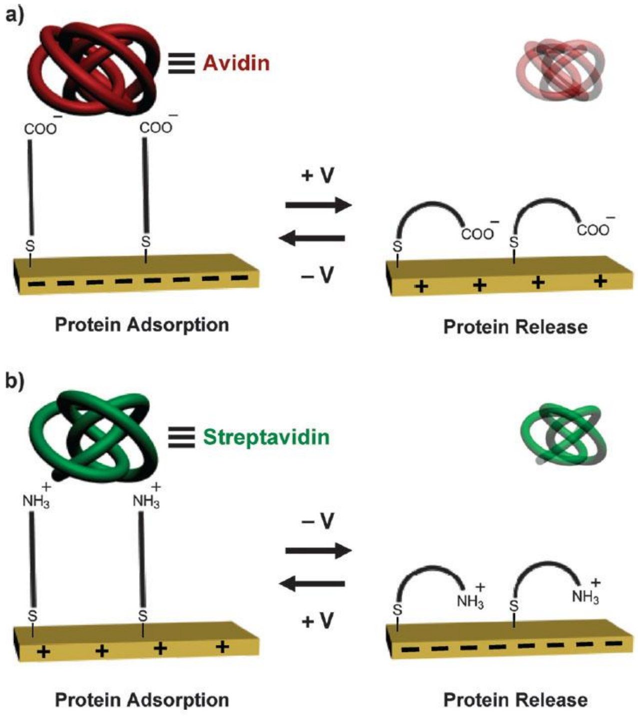
There are also two examples of the non-reversible photochemical switchability control process involving self-assembled monolayer (SAM). Condorelli and co-workers (Sortino 2002) developed a surface that can release nitric oxide for photochemotherapeutic purposes, and Maeda and co-workers (Nakanishi 2004, Nakanishi 2007) prepared a photocleavable surface via UV irradiation for cell adhesion control application.

UV or visible light can be absorbed by skin and cause damage to certain tissues. Due to this limitation, photo-responsive polymers to UV/visible light are not suitable for biomedical applications. Infrared radiation, on the other hand, can penetrate human tissues and minimized the damage caused by irradiation. It is thus more applicable in the photo-responsive drug delivery systems. Fréchet and co-workers (Goodvin 2005) reported a type of micelles comprised by hydrophilic PEG blocks and hydrophobic 2-diazao-1, 2-naphthoquinone segments, which can dissociate with IR irradiation and lead to the release of encapsulated agents.

1.2.4. Electro-Responsive Polymers

Electro-responsive polymers can transform electrical energy into mechanical energy, so they will shrink, swell or bend when an electric field is applied (Filipcsei 2000, Shiga 1997). They are drawing more and more attentions as they may be a type of smart materials for the applications of biomechanics, sensors, energy transduction, artificial muscle actuation, chemical separations, sound dampening and controlled drug delivery systems (Shiga 1997, Kim 1999, Kulkarni 2007, Bajpai 2008, Ramanthan 2001). Usually, polyelectrolytes are used for electro-responsive polymers (Kim 2004). The deformation of polyelectrolyte gels can be induced by applying an electric field. The gels swell or deswell due to anisotropic movements of charged ions towards the anode or cathode. There is a type of polythiophene-based switchable gels that can generate a pressure of 10 kPa when swell and deswell in a confined well. It can be used in small-scale actuators or valves in microscaled systems (Irvin 2001).

Many natural and synthetic polymers have been employed to prepare electro-responsive materials, such as chitosan, chondroitin sulfate, hyaluronic acid, alginate, vinyl alcohol, allylamine, acrylonitrile, 2-acrylamido-2-methylpropane sulfonic acid, aniline, 2-hydroxyethyl methacrylate, methacrylic acid, acrylic acid and vinyl sulfonic acid (Jensen 2002, Sutani 2001, Homma 2000, Lin 2008, El-Hag Ali 2006). A synthetic IPN reported by Kim and co-workers (Kim 2004) composed of poly(2-hydroxylethyl methacrylate) and chitosan can bend under an electric field. The influence of ionic strength and applied voltage to the bending rate and angle are also studied in the same report.



Scheme 1.5: Electrically controlled adsorption and release of avidin and streptavidin proteins by low density ionisable alkanethiolate SAMs on gold surfaces (Mu 2007)

Kong and co-workers (Mu 2007) successfully incorporated two different types of low density SAMs with microfluid chips to control the adsorption and release of two proteins with different isoelectric points. As shown in Scheme 1.5, acid-ended and amino-ended monolayers showed reversible and different conformational reorientation behavior under positive and negative potential. Under electrical control, the proteins with different charges can be reversibly and selectively adsorbed and released from the switchable surfaces.

1.2.5. CO_2-Responsive Polymers

CO_2-responsive gels have been used in cleaning of artwork (Caretti 2010). The uses of aqueous, nonaqueous, and mixed gels have increased enormously for the purpose to remove varnish and overpainting from paint surfaces (Wolvers 1989), stains from stone (Wheller 2005) and stains and adhesives from papers (Sarda 2007). Gels can sequestrate solvents in their matrices to minimize damages of using liquid for cleaning paint surfaces and to bring some other advantages (Caretti 2010). For example, the active solvent can be slowly released from the gel/coating interface which reduces the risk of swelling paint layers. The gels can accommodate different solvents (Cremonesi 2000) and encapsulate different cleaning agents like enzymes (Wolbers 2000), chelating molecules and microemulsions (Carretti 2009, Carretti 2007, Carretti 2003), which makes the gel-based cleaning technique useful in cleaning frescoes (Borgioli 2001), glasses (Valentin 1996), metals (Tomozei 1998) and even feathers (Da Silveira 1998) beside paint on wood or canvas. The gels with solvents of different polarities could remove stains of varied nature, especially old varnishes, such as gels with poly(vinyl alcohol)-borax formulations (PVA-B) as gellant (Carretti 2009) and "solvent gels" (Wolbers 1989).

To clean and remove degraded varnishes from surfaces of artwork, a type of CO_2 responsive rheoreversible gels with low molecular mass organogelators (LMOGs) has been developed (Terech 1997, Weiss 2006, George 2006, Abdallah 2000). It can be transformed between free-flow liquid and gel forms reversibly and without heating. By making carbon dioxide gas passing through a solution with a low concentration of an amine LMOG, gelation occurs spontaneously and ammonium carbamate forms (eq 1) (Carretti 2010). When a displacing gas, for example, nitrogen is passing through the gel, it could be reverted to free-flowing liquid again at room temperature or slightly elevated temperature (eq 1).

$$CO_2 + 2RH_2N \underset{N_2}{\rightleftarrows} NRH_2CO_2^-H_3RN^+ \qquad (1)$$

In the gel system where the polarity is relatively low, the positive charges of ammonium groups and negative charges of carbamate ions form a self-aggregated fibrillar network (SAFIN) in favor of reduced free energy. At the same time, SAFIN can immobilize the liquid component macroscopically (Weiss 2006). Most of the liquid in the network can diffuse microscopically through the varnish or overpaint layer to the paint layer as they would in the absence of the gel. A dynamic interaction between the liquid and the surface makes it is possible to do the cleaning work using the gels (Weiss 2006). Solvents with a wide range of polarities can be located at upper layers of a paint surface and be removed from the paint surfaces with LMOG in analogue to a liquid with cotton. It can minimize the residual cleaning agent after treating the gels with displacing gas.

In addition, some researchers replaced the LMOG with commercially available polymers such as polyallylamine (PAA) (Carretti 2003, Carretti 2005) and polyethylenimines (PEI) (Carretti 2008). These polymers have many advantages, such as availability in large quantities, having the same chemistry shown in eq 1, solubility in many solvents commonly used as a cleaning agent, cross-linking more easily between the polymer chains than LMOG, a slower diffusion rate into a paint layer than that of LMOG and longer stability periods than contact times for cleaning a paint surface (Carretti 2010). To remove the cleaning gels more easily, an alternative strategy was reported (Carretti 2005, Carretti 2008). By adding a small amount of a very dilute acid aqueous solution, the gels will be transformed to free-flow liquid, which could be removed with minimum residue left.

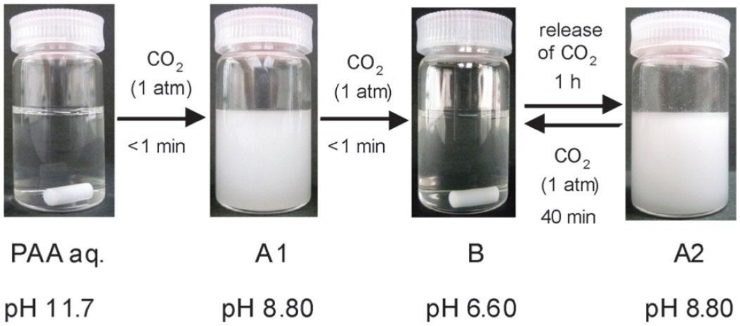


Figure 1.5: Photographs of PAA solution after the addition of CO_2 (A1), further addition of CO_2 (B), and release of CO_2 (A2) (Nagai 2011)

A recent report (Nagai 2011) found that by bubbling CO_2 into a polyallylamine (PAA) aqueous solution and release CO_2, the pH of the solution could be changed, and a reversible polymer chains association/dissociation process was observed. This CO_2-resonsive crosslinking/decrosslinking behavior of PAA is shown in Figure 1.5.

Another type of very important CO_2 responsive materials, amidine containing materials in the forms of both small molecules and polymers will be introduced in the following part of this chapter.

1.2.6. Other Stimuli Responsive Polymers

Some other stimuli-responsive polymers become increasingly important and get more and more attention in biomedical applications, for example, biochemically-responsive, magneto-responsive, ultrasound-responsive polymers (Roy 2010, Theato 2008, Podual 2000, Ulijin 2006, Oh 2007, Wang 2006, Marmottant 2003).

Some of the more commonly considered stimuli are very challenging for in vivo biomedical applications. For biochemically-responsive materials, they have the advantages of responses to stimuli like biological small molecules or macromolecules present in natural living systems (Roy 2010, Theato 2008). So far, several types of biochemically-responsive systems have been developed, based on the following polymers: glucose-responsive polymers (Gil 2004, Ito 1989, Podual 2000, Brownlee 1979, Miyata 2002), enzyme-responsive polymers (Thornton 2005, Ulijin 2006), antigen-responsive polymers (Lu 2003, Miyata 1999) and redox/thiol-responsive polymers (Oh 2007, Tsarevsky 2002). These systems offer opportunities for researches to develop novel biological sensors, smart surfaces and controlled delivery release systems (Mendes 2008, Roy 2010).

Magneto-responsive polymer can respond to magnetic fields so that the free chains in solution can be attached to surfaces or crosslinking networks as the field is switched on and off (Roy 2010). Most of the reports about magneto-responsive polymers involved crosslinked networks with inorganic magnetic particles physically entrapped or covalently immobilized in them (Szabo 1998, Szabo 2000). In the presence of a non-uniform magnetic field, the polymer networks would experience reversibly and instantaneously changes in their size and shape (Zrinyi 1997, Wang 2006). While in the presence of a uniform magnetic field, the particle-particle interaction leads to particle assembly in the polymer networks and transformations of material properties (Roy 2010). Due to safety reason to living creatures, magneto-responsive polymers also received significant attention in biomedical applications such as drug delivery systems, cancer therapy agents, sensors, biomimetic actuators and so on (Zrinyi 2000, Starodoubtsev 2003, Babincona 2001).

Ultrasound-responsive materials are also very attractive to the application of controlled drug delivery and release due to the fact that ultrasound is a type stimulus which can be noninvasive and externally localized (Kost 1992). The mechanism of the ultrasound-responsive polymer is cavitation. The gas-filled microbubbles incorporated with self-assembled polymers and imploded eventually due to the ultrasound energy.

Under this effect, polymer assemblies could be disrupted and released the encapsulated therapeutic agents at a certain location in vivo (Marmottant 2003).

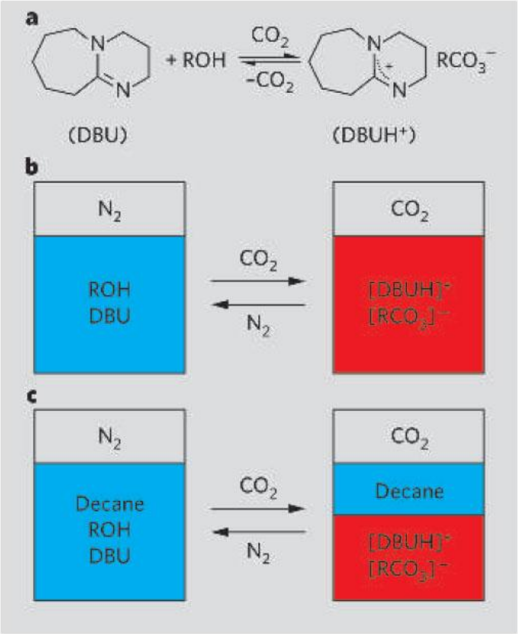
1.3. Amidine Chemistry

In organic chemistry, a base is generally defined as a reagent which can abstract protons and yield a carbanion species (Ishikawa 2009). In textbooks, organobases are usually limited to amines, which are considered as weak bases according to the definition of bases. As one of the derivatives of amines, amidines are iminoamnes built from two nitrogen-containing functionalities, one imine function group (=NH) and one amine group. Due to the more basic amine species, amidines and some other amine derivatives with exceptional basicity are stronger bases and so called organosuperbases (Ishikawa 2009, De Wolfe 1975, Shiriner 1944).

From the view of the physical-organic field, the most attractive physicochemical property of organosuperbases is the high basicity associated with high kinetic activity in proton exchange reactions (Ishikawa 2009). Several solvents have found to be appropriate media to study the basicity of strong bases, including acetonitrile, dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) (Ishikawa 2009). The pK_a values of many amidines with different substituents have been measured (De Wolfe 1975). A number of amidines have been widely used as bases and/or nucleophiles in organic synthesis, especially as a catalyst. Two amidines with relatively stronger basicity are commercially available, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicycloundec-7-ene (DBU) (Ishikawa 2009). Amidines (cyclic or non-cyclic) can be synthesized by several methods, including condensation of 1,2-diamine, coupling of imines, modification of amide derivatives, oxidative amidination, ring opening reactions of aziridine and so on (Ishikawa 2009, De Wolfe 1975, Shiriner 1944).

1.3.1. CO_2 Switchable Solvents

To reduce the release of volatile organic carbons (VOCs) to the environment, the cost burdens of the reduction of solvent usage and to replace organic solvent with benign alternatives, supercritical CO_2 ($scCO_2$), water, ionic liquids (ILs), gas expended liquids (GXLs) and switchable solvents have drawn much more attention (Jessop 2007, Backman 2002, Li 1997, Wasserscheid 2002, Jessop 2005).



Scheme 1.6: The switching of a switchable solvent DBU (Phan 2008)

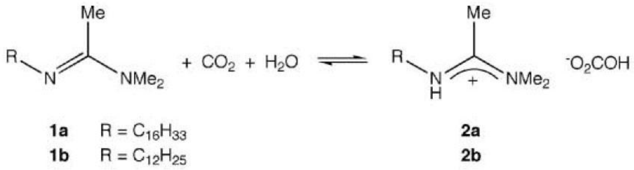
Among these options, switchable solvents are especially fascinating due to their reversibly switchable properties upon command. Jessop and coworkers (Jessop 2005, Phan 2008, Phan 2009) reported a reversible nonpolar-to-polar solvent, which can be switched by CO_2 and N_2 or argon in the presence of alcohol as shown in Scheme 1.6. The non-ionic liquid is as nonpolar as chloroform, while it is as polar as DMF or propanoic acid under CO_2 (Jessop 2005, Phan 2008, Phan 2009). A series of switchable solvent consisting different amidine/alcohol and guanidine/alcohol mixtures using CO_2 as switches were also reported (Pham 2008, Heldebrant 2010, Jessop 2010).

Polystyrene synthesis was carried out in DBU/PrOH mixture to show the utility of the solvent switchable property. After polymerization, the polymer particles could be precipitated by bubbling CO_2 to switch the solvent to its ionic form. After the polymer was filtered, the switchable solvent could be recovered and switched to its neutral form by N_2 for reuse (Phan 2008). Another example of the application of switchable-polarity solvents (SPS) is the extraction of soybean oil from crushed soybeans (Phan 2009). Using this SPS instead of hexane will cause several advantages. There will be no significant solvent loss occur, since no volatile solvent involved. There is no distillative removal of the solvents needed, or the enormous energy consumption. After the oil removed from high polarity PSP as a separated phase, the solvent can be switched back to low polarity PSP and reused since the polarity changes are reversible.

Beside the polarity switchable organic solvents, Jessop and co-worker reported a type of "switchable water" due to the unsustainable current salting-out method of separating water-soluble organic compounds from water (Mercer 2010). In the presence of diamine, the aqueous solution has zero ionic strength. After reacting with CO_2, it has higher ionic strength than before, which can salt out THF from water. This process is reversible and allows reuse the aqueous solution (Mercer 2010).

1.3.2. CO_2 Switchable Surfactants

Surfactants can stabilize emulsions that have important applications in emulsion polymerizations, cleaning metals, viscous oil transportation, oil-recovery and cosmetics (Meyer 2008, Austad 2000, Masliyah 2004, Liu 2006, Fowler 2011). However, surfactants are only useful in some certain stages during these processes. After those stages, surfactants could become a problem during the separation and purification of the components (Liu 2006). Switchable surfactants became a satisfactory solution to the problem. Emulsions could be stabilized by an active form of the surfactants when needed and be destabilized afterward by switching off the surfactants to its inactive forms, or vice versa. Because the switch process is reversible, the surfactants can be recovered and reused (Liu 2006).



Scheme 1.7: The reversible switching of an alkyl chain amidine (Liu 2006)

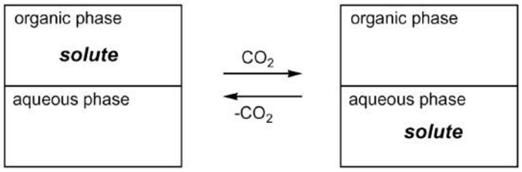
Jessop and co-workers (Liu 2006) reported a type of reversible switchable surfactant triggered by mild and inexpensive stimuli, CO_2 and argon (or N_2). The structure and switching process is shown in Scheme 1.7.

When the surfactants were mixed with crude oil and water, a mixture of low viscosity formed under CO_2. By switching the surfactant to demulsifier with argon, the oil and water separated into two phases. This is a significant progress in the application of surfactants in crude oil transport and recovery industry (Liu 2006). Another example of the application of switchable surfactants is about latex. When 4% of the surfactant was present in the synthesis of styrene latex, the resulted latex could be stabilized under CO_2 and precipitated when the surfactants are switched off by argon or N_2 at 65 °C (Liu 2006).

In another work, switchable surfactants and amidine containing initiator were used as the same to obtain polystyrene and poly(methyl methacrylate) colloidal latexes with better properties (Fowler 2011). The resulted polymer latexes can be more stable under CO_2 and be destabilized by removing CO_2 with heat and air bubbling. The precipitated polymer particles can be collected by filtration and then dried to yield polymer powder. The remnant aqueous phase was clear (Fowler 2011).

1.3.3. CO_2 Switchable Solutes

In green chemistry, the post-reaction separation with environmental friendly method is preferred. So solutes with controllable partitioning between organic and aqueous phases can help to achieve this goal. If reagents or byproducts could be tagged by amidine, the excess unreacted part or the unwanted product can be removed easily by a benign switching agent CO_2, trace amount of H_2O and N_2 or air.



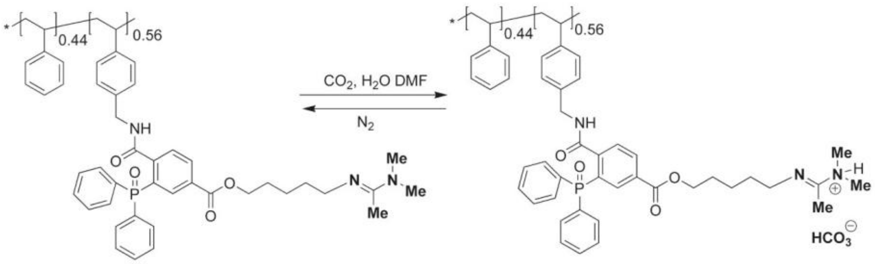
Scheme 1.8: Switching the solutes's partitioning behaviour (Phan 2009)

An amidine-tagged chelating agent used for catalyst recovery was reported (Desset 2009). Jessop and co-workers (Phan 2009) synthesized a hydrophilicity-switchable solute with high partition coefficient using N,N-dimethylacetamide dimethyl acetal and an amine bearing dye. First the amidine containing dye was dissolved in the organic phase, and it can be switched to partition in the aqueous phase and back into the organic phase reversibly. The controllable partitioning is demonstrated in Scheme 1.8. The partitioning process was confirmed by pictures took under short-wave UV illumination (Phan 2009).

Similarly, some chemicals with amine groups can be synthesized without effluence of their properties, which can facilitate cleaner reactions and less cost-and energy-requiring separation processes.

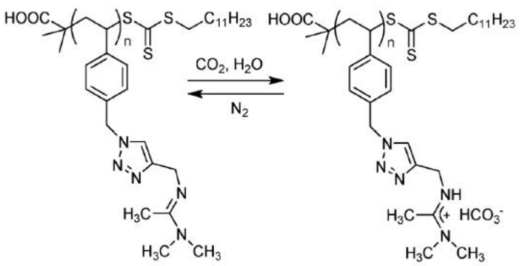
1.3.4. CO_2 Switchable Polymer Materials

In 2009, Wu and co-workers (Zhou 2009) first reported the synthesis of poly(p-azidomethylstyrene)-co-(polystyrene) (PAMS-co-PS) copolymers with amidine pendant groups (shown in Scheme 1.9). They also exemplified the switchability of the polymer in THF and DMF by conductivity and laser light scattering (LLS) tests. The results indicated that by bubbling CO_2 and N_2 alternatively, the polymer underwent a neutral-charged-neutral transition in solution.



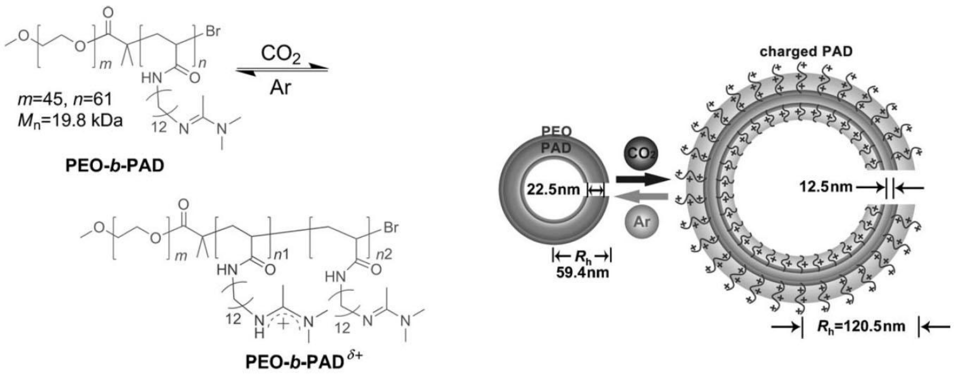
Scheme 1.9: Reversible change between P("amidine"MS)-co-PS and its charged state in DMF with 0.5% H_2O after alternating bubbling of CO_2 and N_2 (Zhou 2009)

Recently, Zhang and co-workers (Guo 2011) synthesized an amidine-based polymer by reversible addition-fragmentation chain transfer (RAFT) polymerization and "click" chemistry method. They tested the switchability of this polymer in different solvents in the presence of CO_2 and N_2. The structure of the polymer and its reaction with CO_2 is shown in Scheme 1.10.



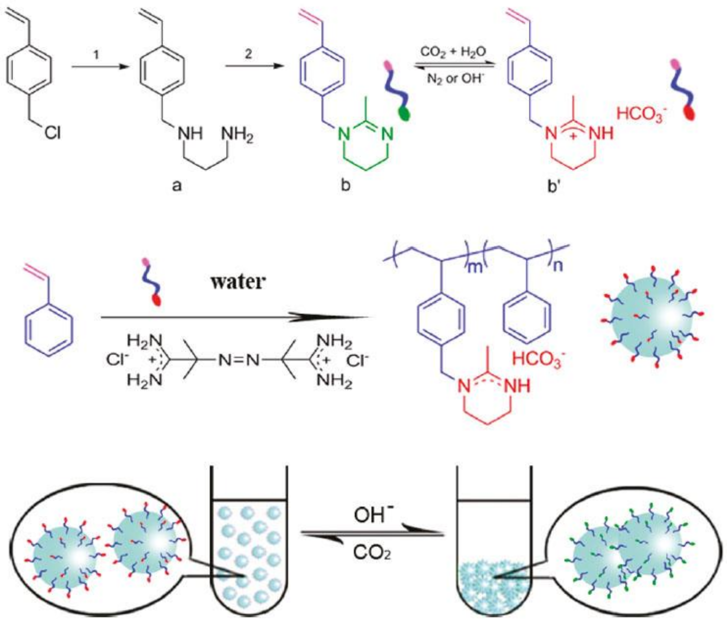
Scheme 1.10: The structure of amidine-based polymer and its reaction with CO_2 and water (Guo 2011)

There are also researchers focusing on the application of amidine-based polymers (Yuan 2011, Zhang 2011). Yuan and co-workers (Yan 2011) reported a type of "CO_2-responsive polymeric vesicles that breathe". First, a difunctional monomer containing acrylic and amidine groups (N-amidino) dodecyl acrylamide (AD) was synthesized. Then a diblock copolymer PEO-b-PAD was prepared. In aqueous solution, PEO-b-PAD formed vesicles due to the existence of hydrophilic PEO blocks and hydrophobic PAD blocks. In the presence of CO_2, the polymer was still amphiphilic, but with different configuration relative hydrophilic and hydrophobic blocks: ionized PAD blocks became more hydrophilic than PEO and turned to the outer layer of the vesicles. At the same time, the sizes of the vesicles increased. When the vesicles were treated with argon, they were switched back to the original form. During the reversible switch process, the size of vesicles increased and decreased in correspondence of the gas used. It looks as the vesicles can inhale CO_2 and exhale N_2 which is shown in Scheme 1.11 (Yan 2011).



Scheme 1.11: Gas-switchable structural change of amidine-containing diblock copolymer PEO-*b*-PAD (left) and schematic representation of its self assembly into vesicles and their reversible gas-responsive "breathing" in aqueous media (right) (Yan 2011)

Another report of a fascinating and important of application of amidine containing polymers is the preparation of reversibly coagulable and redispersible latexes (Zhang 2011). After a switchable monomer was synthesized, the bicarbonate salt of the monomer was copolymerized with styrene to yield a polystyrene-based latex system. A water-soluble and amidine containing initiator was used, as well. As shown in Scheme 1.12, the stable emulsion could be precipitated by adding a small amount of caustic soda and redispersed by adding CO_2. This process can be repeated several times without destroying the polymer latex particles (Zhang 2011).



Scheme 1.12: Synthesis routes of switchable amidine copolymer and its emulsion polymerization with styrene, as well as a sketch of reversible coagulation and redispersion of polystyrene latex triggered by CO_2 and a small amount of caustic soda (Zhang 2011)

Compared to the previous report (Liu 2006, Fowler 2011), one significant advantage of this work is reversibly coagulatable/dispersible polystyrene based latex was synthesized. In Jessop and co-workers' work, this space has been left for further improvements: polymeric latex can only be precipitated from the aqueous solution to yield polymer powder, but no consequence reports about redispersing the latex particles. The reversible switchable latex can solve the problems of the cost of latex transportation and remain the property of the latex maximumly.

1.4. Objective and Outline of This Thesis

Here we propose a simple method to synthesize a CO_2-switchable amidine-containing monomers. The synthesis route only involves a one-step reaction, not like the multi-step routes used in the previous reports (Zhou 2009, Guo 2011, Yan 2011, Zhang 2011). Also, due to the high yield, there is no need of further purification to obtain the monomers. Since this is the first time to report synthesis of the monomers, the two monomer structures were examined. The switchability of the two monomers was also investigated. Simplifying the monomer synthesis to a one-step process and avoiding additional purification steps can reduce costs in the synthesis part. The successful synthesis of the switchable monomers may promote the application studies of amidine-based polymers.

Then switchable polymers with different molecular weights were then thehesized via a conventional free radical polymerization mechanism. The structures and molecular weights of the polymers were characterized. The switchability of the polymers was confirmed by conductivity tests in DMSO. The effect of the molecular weight on the polymer switchability in DMSO was also investigated.

Chapter 1 briefly reviewed the synthesis and applications of various types of switchable materials in literatures including inorganic, organic and polymeric materials. Particular attention has been paid to the recent activities related to amidine-based materials.

Chapter 2 describes the methodology and materials used in the synthesis of amidine-based switchable monomers and polymers. The sample preparation and characterization of the monomer and polymers, as well as their switchability tests, are described in details.

Chapter 3 discusses the experimental results including the characteristics and properties of the switchable monomers and polymers. The effects of the molecular weight to the polymer switchability are investigated and discussed.

Chapter 4 provides a conclusion that summarizes the contributions of this thesis work. Provided also are the recommendations for future work.

CHAPTER 2

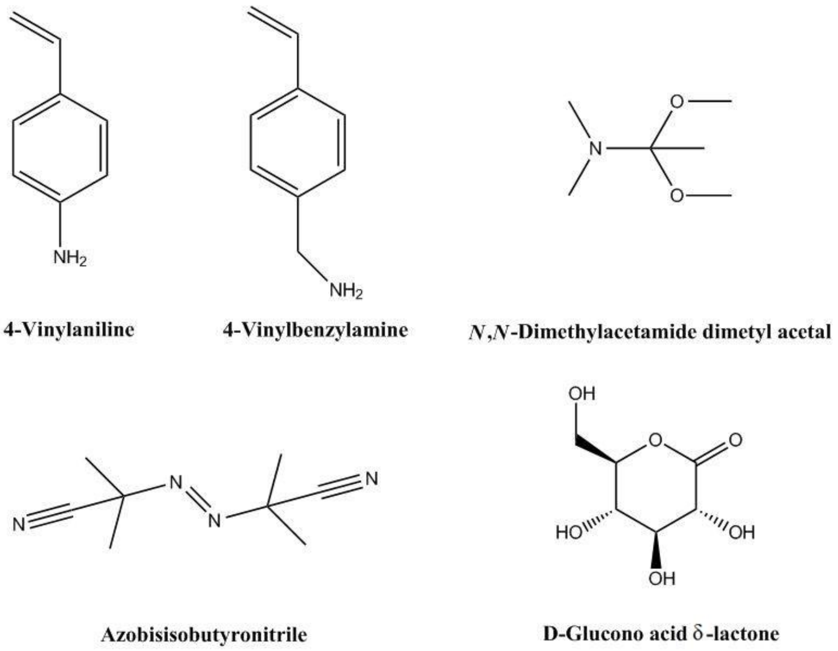
EXPERIMENTAL MATERIALS AND INSTRUMENTATION

2.1. Materials

4-Vinylaniline (97%), N,N-dimethylacetamide dimethyl acetal (90%), toluene (anhydrous, 99.8%) and potassium bromide (KBr) were purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF, reagent, Caledon), N, N-dimethylformamide (DMF, reagent, Caledon), chloroform ($CHCl_3$, reagent, Caledon) and dimethyl sulfoxide (DMSO, reagent, Caledon) were used as received without further purification. N_2 (99.999%) and CO_2 were purchased from Air Liquide Canada Inc. and used as received. Deuterated chloroform ($CDCl_3$, CIL), deuterated water (D_2O, CIL) and deuterated methanol (MeOD, CIL) were used as received. 4-Vinylbenzylamine (92.0 %, TCI America) was used as received without further purification. D-Glucono acid δ-lactone (99.0 %) was purchased from Sigma-Aldrich and used without further purification.

Azobisisobutyronitrile (AIBN) was recrystallized from methanol using the following procedure: AIBN was dissolved in a beaker containing a small amount of methanol at 50 °C. Then the beaker was put into an ice bath for approximately half an hour until no more crystallites formed. The solid/liquid mixture was then poured into a Hirsch funnel lined with filter paper where the solid AIBN crystal was isolated and dried prior to use.

The structures of some of the aforementioned chemicals used in this thesis are shown in Figure 2.1.


4-Vinylaniline 4-Vinylbenzylamine *N*,*N*-Dimethylacetamide dimetyl acetal

Azobisisobutyronitrile D-Glucono acid δ-lactone

Figure 2.1: Structures of some chemicals used

2.2. Experimental Procedures

2.2.1. Synthesis of Monomer

Monomer N,N-dimethyl-N’-(4-vinylphenyl) acetimidamide (DMVPA) was synthesized according to a published procedure (Harjani 2011) with some modifications. A general protocol is: 4-vinylaniline (0.5 g, 4.20 mmol) was added drop-wise to N,N-dimethylacetamide dimethyl acetal (1.23 mL, 8.40 mmol) over 10 minutes at room temperature with stirring. This mixture was allowed to stand for 24 hrs at 65 °C. The methanol byproduct and part of the unreacted N,N-diemthylacetamide dimethyl acetal were removed by rotary evaporator at room temperature. Then the crude product was further dried in a vacuum oven overnight at 40 °C to give the pure product of DMVPA.

Another monomer N, N-dimethyl-N’-(4-vinylbenzyl) acetimidamide (DMVBA), for conductivity comparison studies, was synthesized in the same procedure: 4-vinylbenzylamine (0.5 g, 3.75 mmol) was added drop-wise to N, N-dimethylacetamide dimethyl acetal (1.10 mL, 7.50 mmol) over 10 minutes at room temperature with stirring. The reaction mixture was allowed to stand for 24 hrs at 65 °C. The methanol byproduct and part of the unreacted N, N-diemthylacetamide dimethyl acetal were removed by rotary evaporator at room temperature. Then the crude product was further dried in a vacuum oven overnight at 40 °C to give the pure product of DMVBA.

2.2.2. Synthesis of Polymer

Poly [N,N-dimethyl-N’-(4-vinylphenyl) acetimidamide] (PDMVPA) was synthesized by the conventional free radical polymerization method. A typical procedure is: 500 mg monomer DMVPA, 1 mL DMF and a magnetic stirring bar were transferred into a tube, and a designed amount of AIBN was then added to the tube. The tube was sealed, degassed and put into a preheated oil bath. The polymerization tube was kept at 65 °C for 24 hrs. The polymerization was terminated by pouring the reaction mixture to a beaker containing diethyl ether in excess of more than 100 times of that of the mixture. The precipitated polymer was collected by filtration under vacuum and washed with diethyl ether. The purified polymer was further dried under vacuum in a desiccator overnight.

2.3. Characterization and Testing

2.3.1. Characterization

Nuclear magnetic resonance (NMR) spectra of the monomers DMVPA and DMVBA and polymer PDMVPA were collected from a Bruker AV200 NMR spectrometer. The polymerization conversions of DMVPA were estimated from the ^{1}H NMR results.

The mass spectrometry of $CHCl_3$ solutions of monomer DMVPA and DMVBA were measured using a Micromass GCT flight mass spectrometer. The PDMVPA sample a DMVPA/AIBN weight ratio of 25:1 was measured using a Micromass MALDI MicroMX mass spectrometer.

Fourier transform infrared (FTIR) spectra of 4-vinylaniline, DMVPA and the same polymer sample of MALDI test were collected on a Thermo Nicolet 6700 FTIR spectrometer. To prepare samples for the tests of 4-vinylaniline and DMVPA, two KBr plates were made first. The $CHCl_3$ solution of the two liquid chemical was dropped on a plate. For PDMVPA, a small amount of the polymer was mixed with KBr first, and the mixture was grinded and used to make a plate for the test.

The molecular weights and polydispersity indexes of PDMVPA synthesized with different monomer/initiator ratios were measured by gel permeation chromatography

(GPC) with a system consisting of a Waters 590 HPLC pump, and three Waters ultrastyragel liner columns at 40 °C and a Waters 410 refractive index detector at 35 °C. DMF was used as eluent and narrow polystyrene standards (Waters) were used for calibration of the system.

2.3.2. Switchability Test

The thermal stabilities of bicarbonate salts of the monomer DMVPA and the MALDI test PDMVPA sample were determined by a Netzsch STA-409 Luxx thermo gravimetric analysis (TGA) instrument. The preparation of the samples was as following: CO_2 was bubbled in to vials containing the monomer and the polymer for 12 hrs before sealed and stored under CO_2 atmosphere for 24 hrs. This process was repeated once before the tests.

A second PDMVPA sample was prepared in a different way for comparing the yield of the reaction between polymer and CO_2. Upon the complete polymerization of DMVPA in DMF, CO_2 was bubbled into the reaction solution with stirring for half an hour. The solution was dropped into a beaker containing diethyl ether with a 100-fold in volume of the reaction solution. The precipitated polymer was last filtered and washed by diethyl ether. Then the sample was dried in a desiccator under CO_2 atmosphere before TGA test.

The partitioning of the monomer DMVPA was proved by ^{1}H NMR measurement results. First, 46.6 mg DMVPA was dissolved into a mixture of D_2O and $CDCl_3$. Samples from the two separated layers were collected to run ^{1}H NMR tests, after alternately bubbling with CO_2 and N_2. The same procedure was followed in testing the partitioning of PDMVPA. The PDMVPA sample used in this test was the one synthesized with 25:1 DMVPA/AIBN ratio. 46.6 mg of PDMVPA was dissolved in D_2O and $CDCl_3$. CO_2 and N_2 were then bubbled into the mixture. After each process, samples of in the two separated layers were collected for the ^{1}H NMR tests.

The conductivities of DMSO solutions of the monomer DMVPA (20.7 mM in 12 mL DMSO) and the polymer PDMVPA (46.6 mg in 12 mL DMSO) with different molecular weights were tested by Jenway 4510 bench conductivity meter with bubbling CO_2 and N_2 alternately. For comparison, the conductivity of DMSO solution of the monomer DMVBA (20.7 mM in 12 mL DMSO) was also tested with the same procedure. The conductivity of pure DMSO was tested with as a controlled experiment.

Potentiometric titration was conducted at room temperature using a Mandel PC-titrate system. The 1 mg/mL aqueous solutions of monomer DMVPA and PDMVBA with different molecular weights, as well as monomer DMVBA, were prepared under ultrasonic to make the samples well dispersed. A 2 wt % D-glucono δ-lactone solution was used as titrant. Also pH of the 1 mg/mL solutions of the polymers with different molecular weights are collected after bubbling CO_2 until saturation.

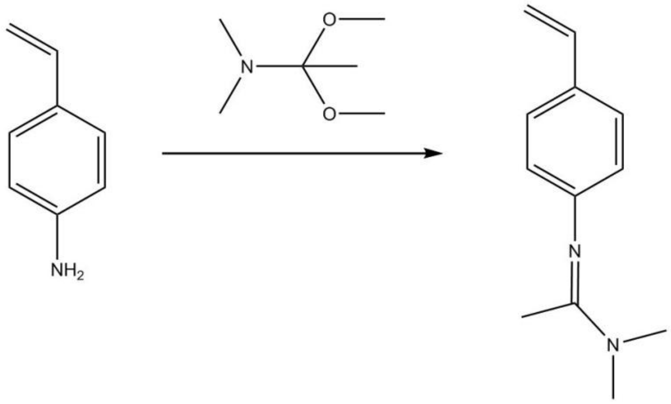
CHAPTER 3

RESULTS AND DISCUSSION

3.1. Synthesis of the Monomers

3.1.1. Monomer DMVPA

The synthesis route for the amidine containing monomer DMVPA is shown in the following scheme. This is the first report of the synthesis of this monomer.



Scheme 3.1: Synthesis route of the monomer DMVPA

Figure 3.1 shows the ^{1}H NMR spectrum of the monomer DMVPA in $CDCl_3$ with the signal of each proton defined. The integration of each peak correlated well to the number of protons in the final product.

The structure of the final product was further proved by a mass spectroscopy test. The molecular weight of the product plus one proton was 189. For a chemical with the chemical structure of $C_{12}H_{16}N_2$, its molecular weight is 188. Both the ^{1}H NMR spectrum and mass spectrum confirmed that the final product was the monomer DMVPA as designed in Scheme 3.1.

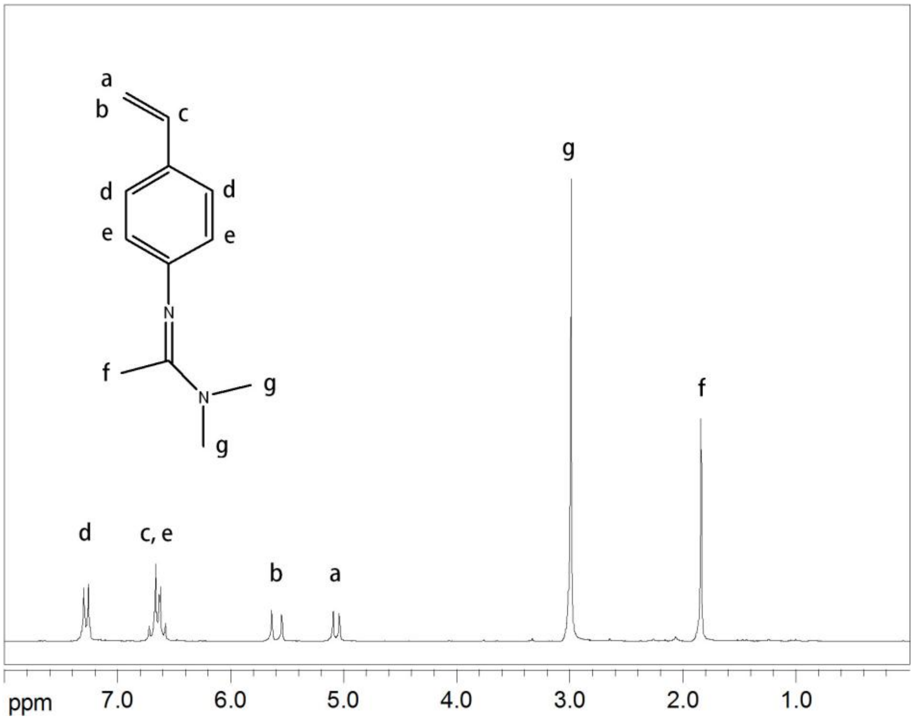


Figure 3.1: ^{1}H NMR spectrum of monomer DMVPA in $CDCl_3$

The ^{1}H NMR spectra of the reactants N,N-dimethylacetamide dimethyl acetal, 4-vinylaniline and the crude product (the product collected after rotary evaporation of the reaction mixture) are compared in Figure 3.2. Because the excessive N,N-dimethyl-acetamide dimethyl acetal has a high boiling point (118 °C), the unreacted N,N-dimethylacetamide dimethyl acetal could not be removed by rotary evaporator. So by comparing to the spectrum in Figure 3.2 a, there were still the signals of protons belonging to the unreacted N,N-dimethyl-acetamide dimethyl acetal in the spectrum of the crude product (Figure 3.2 c). The signals of the hydrogen atoms of the vinylbenzyl group in the reactant 4-vinylaniline and DMVPA overlapped in the spectrum of the crude product.

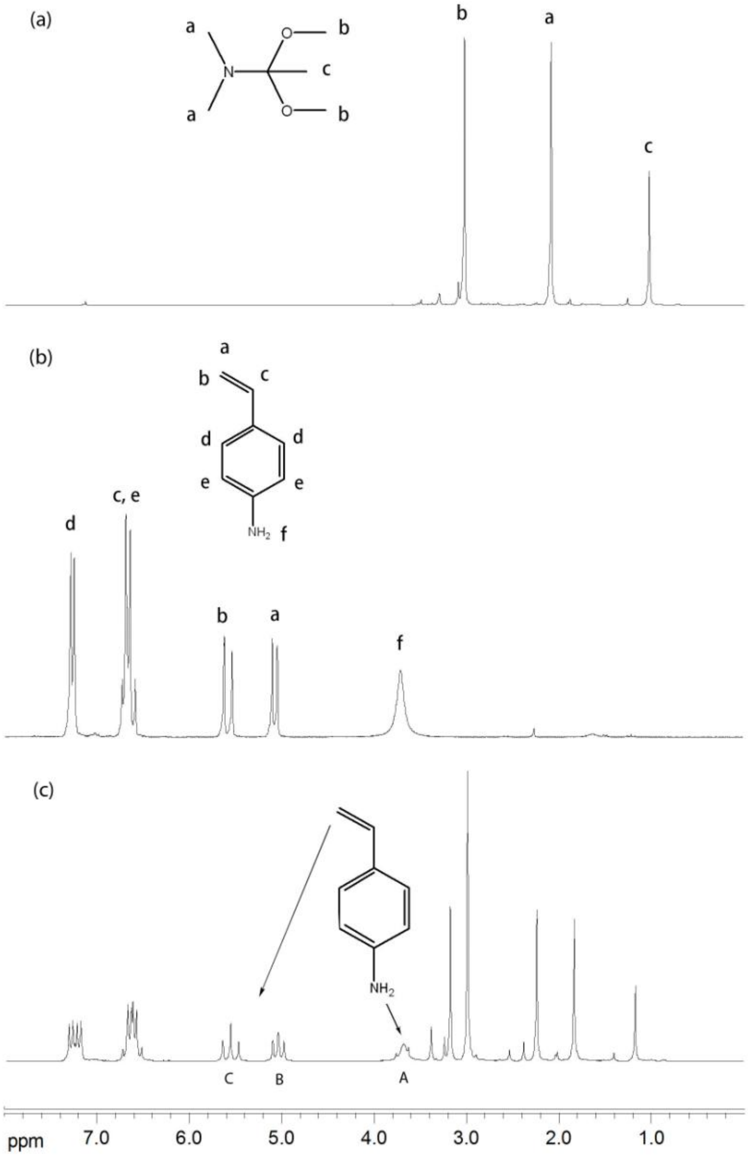
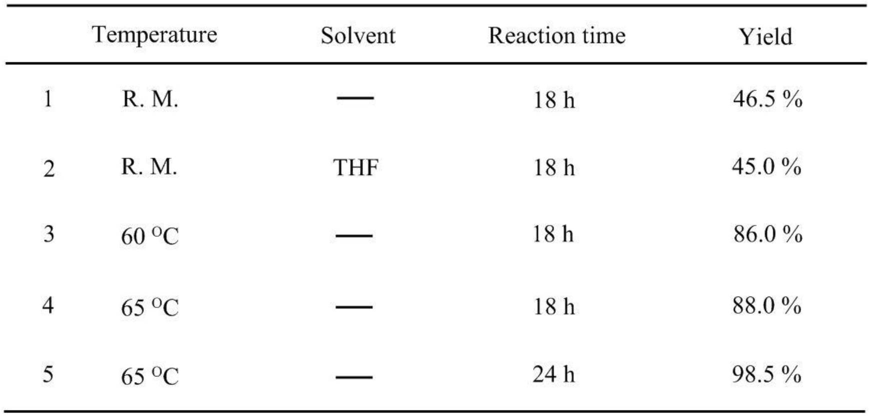


Figure 3.2: ^{1}H NMR spectra of the reactants N, N-dimethylacetamide dimethyl acetal (a), 4-vinylaniline (b) and the crude product (c) in $CDCl_3$

From the area ratios of the peaks belonging to the amine group of the unreacted 4-vinylaniline (about 3.75 ppm, peak A) and one of the hydrogen atoms of the methylene of the double bond both in 4-vinylaniline and the product (about 5.03 ppm, peak B or 5.58 ppm, peak C), the amount of the residual 4-vinylaniline can be calculated to give the yield of the monomer product (as shown in Table 3.1). For example, in Figure 3.2 c, the area ratio of peak A and the triplet peak B. Because amine group has two hydrogen atoms, so the percentage of the residue 4-vinylaniline in the total amount of 4-vinylaniline and DMVPA is half of 1.07, which was 53.5 %. The respective yield of DMVPA was 46.5 %.

Table 3.1: Yield in the synthesis of DMVPA under various conditions



	Temperature	Solvent	Reaction time	Yield
1	R. M.	—	18 h	46.5 %
2	R. M.	THF	18 h	45.0 %
3	60 ^{O}C	—	18 h	86.0 %
4	65 ^{O}C	—	18 h	88.0 %
5	65 ^{O}C	—	24 h	98.5 %

DMVPA was synthesized under various conditions targeting for a high yield. Because 4-vinylaniline is a liquid, the reaction between amine group and N,N-dimethylacetamide dimethyl acetal can occur at room temperature without solvent according to a literature report [1]. The first reaction in this work was carried out at room temperature and with no solvent for 18 hrs. The yield was relatively low (46.5 %).

Adding THF as a solvent at room temperature did not help to increase the yield. Higher temperature and longer time had been tried. Eventually, a yield of 98.5 % was obtained from the reaction at 65 °C for 24 hrs. The crude product was purified in a vacuum oven at 40 °C overnight.

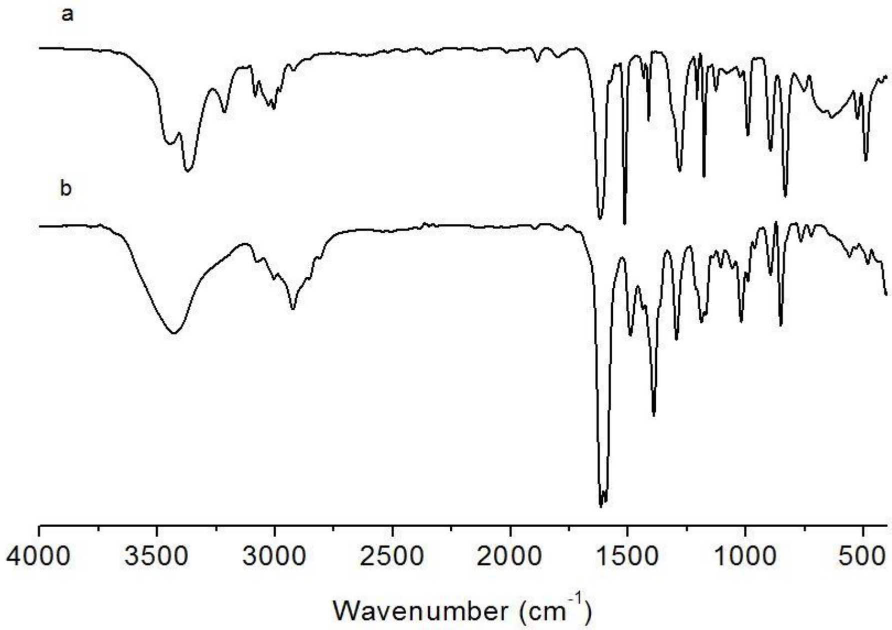
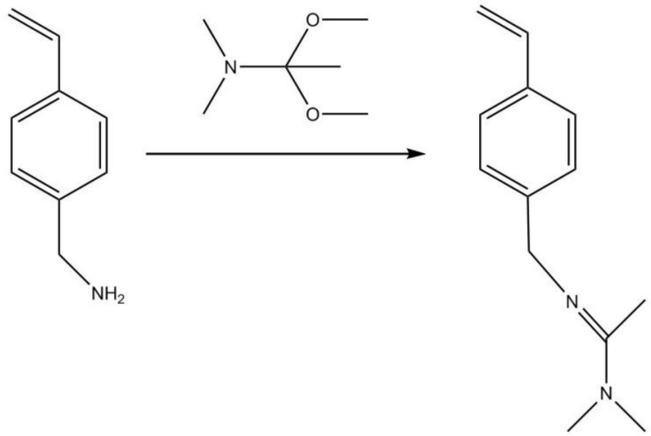


Figure 3.3: FTIR spectra of reactant 4-Vinylaniline (a) and monomer DMVPA (b)

In the FTIR spectrum of 4-vinylaniline (Figure 3.3 a), the signals at 3440 and 3350 cm^{-1} belonged to the asymmetrical and symmetrical hydrogen bonded primary amine coupled doublet and N-H stretching. The signals at 3200 and 1620 cm^{-1} were the Fermi resonance bands and N-H bending. In the spectrum of DMVPA (Figure 3.3 b), these signals disappeared except for the signal of hydrogen bonds due to the primary amine group reacted with N,N-dimethylacetamide dimethyl acetal and transformed into an amidine group. The signals of aromatic C-H stretching and C-H stretching of double bonds around 3050 cm^{-1}, C-C ring stretching around 1600, 1500 and 1468 cm^{-1}, C-N stretching around 1280 and 1175 cm^{-1}, o-disubstituted benzenes around 735-770 cm^{-1} and C-H out-of-plane bending of double bonds around 985-995 and 900-940 cm^{-1} remained the same after 4-vinylaniline reacted with N,N-dimenthylacetamide dimethyl acetal. The FTIR spectra showed that the reaction took place successfully.

3.1.2. Monomer DMVBA

DMVBA was synthesized (shown in Scheme 3.2) for a comparison study with DMVPA in conductivity tests.



Scheme 3.2: Synthesis of the monomer DMVBA

The structure of DMVBA was confirmed by the 1H NMR spectrum (Figure 3.4). Furthermore, the result of the mass spectroscopy test of DMVBA was 203, which is the molecular weight of a compound with a chemical structure of $C_{13}H_{18}N_2$ plus one proton.

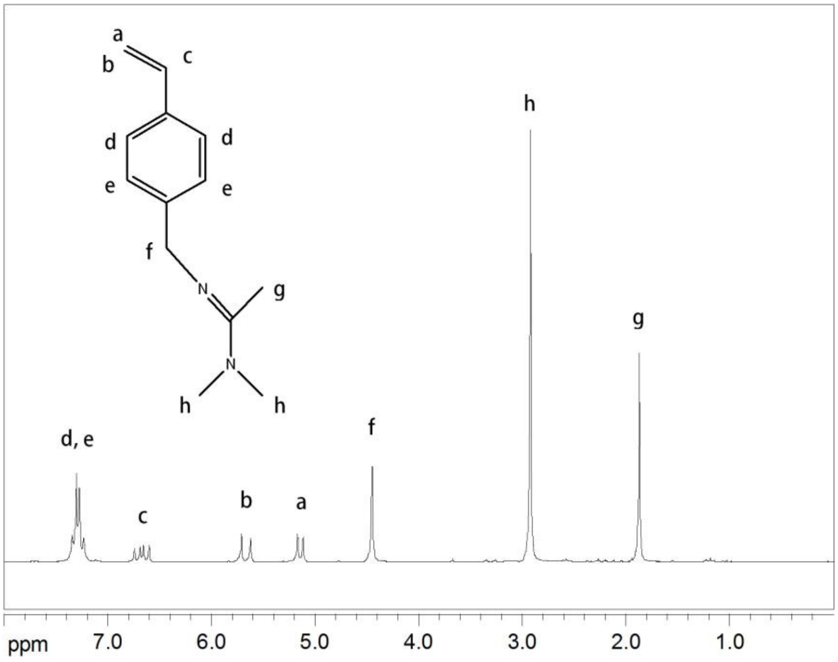
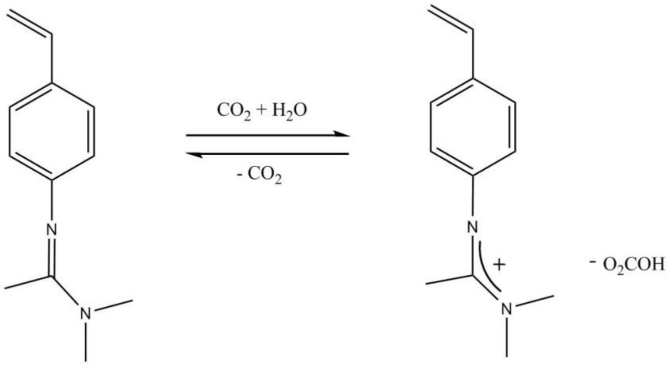


Figure 3.4: ^1H NMR spectrum of the monomer DMVBA in $CDCl_3$

3.1.3. Switchability Test of the Monomers

The anticipated reaction of the amidine containing monomers protonated by CO_2 and deprotonated by N_2 is shown in Scheme 3.3.



Scheme 3.3: Protonation and deprotonation of the monomer DMVPA

However, in this work, it has been found very difficult to obtain the bicarbonate salt in a solid form of DMVPA as described in the literature report (Harjani 2011). After bubbled CO_2 through ether or acetonitrile solution of the monomer DMVPA and kept in the freezer for 24 hrs, we only observed increased viscosity but collected no precipitants. CO_2 was bubbled into the liquid monomer. This liquid was stored under CO_2 atmosphere before the TGA test. The theoretical weight loss for the monomer DMVPA with the purity of 98.5% should be 22.53%. From the TGA curve (Figure 3.5), a change in weight of -19.08% was observed from room temperature to about 300 °C at which the thermo decomposition process of the monomer started. The TGA result showed that not all the monomer reacted with CO_2 during the sample preparation. There was about 84.7 mol% of the monomer transformed into its bicarbonate salt form. The TGA result also reflected that the thermal stability of DMVPA was very good. It could be attributed to a conjugation structure between the benzene ring and amidine group.

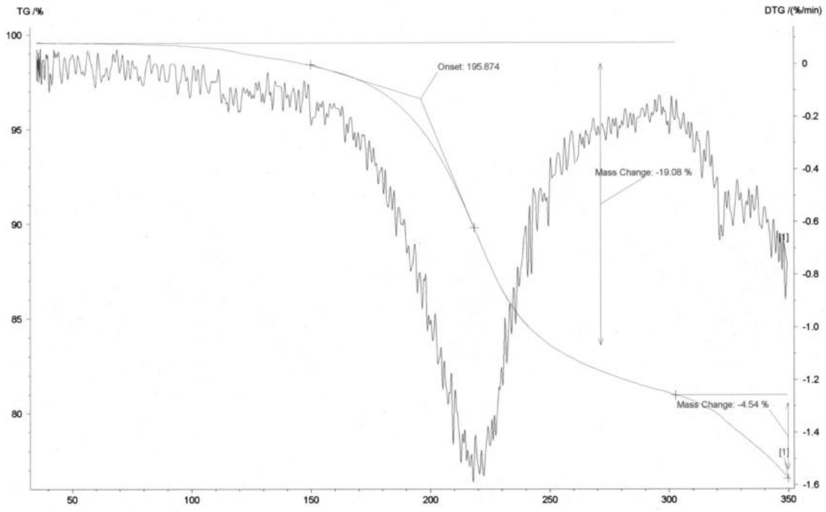


Figure 3.5: TGA trace of the bicarbonate salt of DMVPA

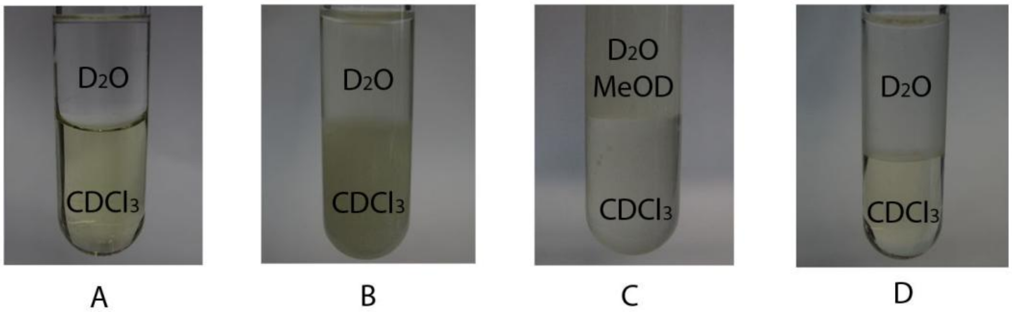


Figure 3.6: Pictures of the monomer DMVPA partitioning in D_2O and $CDCl_3$: DMVPA in mixture of D_2O and $CDCl_3$ (A); after CO_2 bubbling (B); bicarbonate salt of DMVPA in the mixture of D_2O, MeOD and $CDCl_3$ (C) and after N_2 bubbling and evaporation of MeOD (D)

The partitioning of DMVPA in a mixture of $CDCl_3$ and D_2O was tested. In a tube, DMVPA was dissolved in $CDCl_3$, followed by the addition of D_2O. The tube was shaken and then stored in refrigerator overnight to allow the mixture settle and separate. The recovered D_2O phase was colorless, and the chloroform phase was in yellow (Figure 3.6 A). Figure 3.7 shows the ^1H NMR spectra of the organic and aqueous phases. DMVPA only dissolved in $CDCl_3$, even after shaking the tube to mix the two phases.

The aqueous phase and the organic phase samples were transferred back to the tube and CO_2 was bubbled through the mixture for about one hour. The bottom layer became unclear while the upper aqueous layer became pale yellow (Figure 3.6 B). For further investigation, the aqueous layer was collected for ^1H NMR test. CO_2 was bubbled into the organic layer again for a prolonged time to evaporate all $CDCl_3$. Then the residue was dissolved in MeOD for ^1H NMR test (Figure 3.8). These results suggest that the bicarbonate salt formed which was not soluble in $CDCl_3$ but had a low solubility in D_2O and a good solubility in MeOD. In a comparison study, the bottom layer mixture of

$CDCl_3$ was collected and filtered twice with a 0.2 µm syringe filter. A clear, pale-yellow coloured liquid was obtained and tested by ^1H NMR. The result showed that there was still some monomer which did not react with CO_2 and was dissolved in $CDCl_3$.

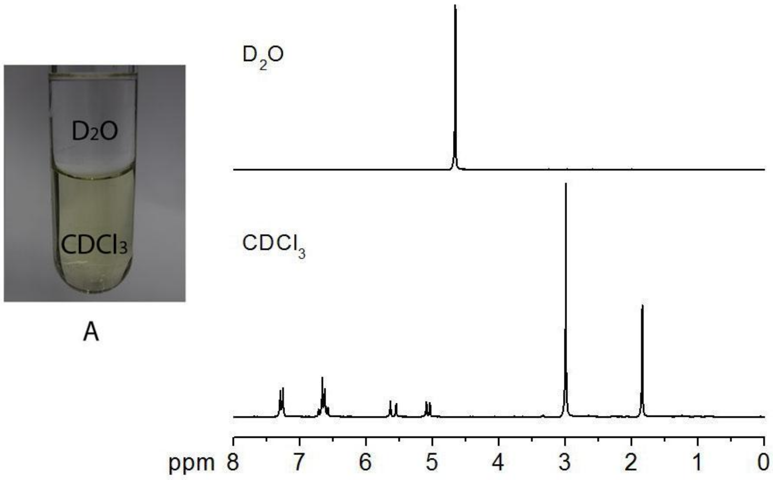


Figure 3.7: ^1H NMR spectra of the aqueous and organic phases with the monomer DMVPA dissolved in mixture of D_2O and $CDCl_3$

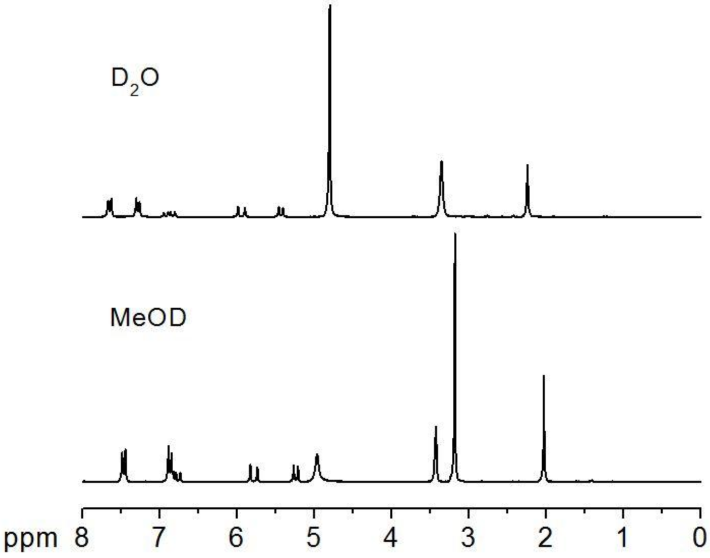


Figure 3.8: ^1H NMR spectra of the bicarbonate salt of DMVPA in D_2O and MeOD

Further to investigate the yield of the reaction between the monomer DMVPA and CO_2, a ^{1}H NMR test of the natural form DMVPA was carried out (Figure 3.9). The two insert signals around 6.50 to 6.80 ppm showed that, in the spectrum of the bicarbonate salt of DMVPA, the peaks of the two protons of the carbons next to the amidine substituted carbon of the benzene ring (proton “e” in Figure 3.2) were shifted about 0.07 ppm towards the higher field. But in the spectrum of bicarbonate salt of DMVPA, the signals of the natural form DMVPA were too weak to be detected.

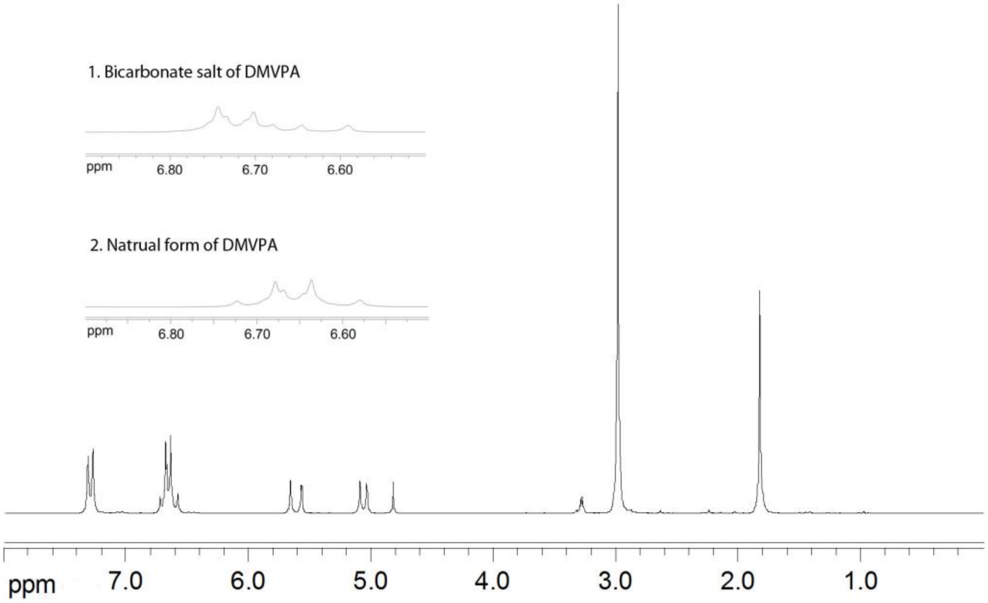


Figure 3.9: ^{1}H NMR spectra of the monomer DMVPA in MeOD, the inserts are the amplified signals from 6.50 to 6.90 in Figure 3.8 (1) and 3.9 (2)

After the ^{1}H NMR tests, all the samples in D_2O and MeOD were collected back to the tube and some $CDCl_3$ was subsequently added. The upper layer was the mixture of D_2O and MeOD, in a yellowish color; while the bottom layer was $CDCl_3$ with a very pale yellowish color (Figure 3.6 C). It also showed that there was a small amount of unreacted natural form of the monomer DMVPA dissolved in $CDCl_3$.

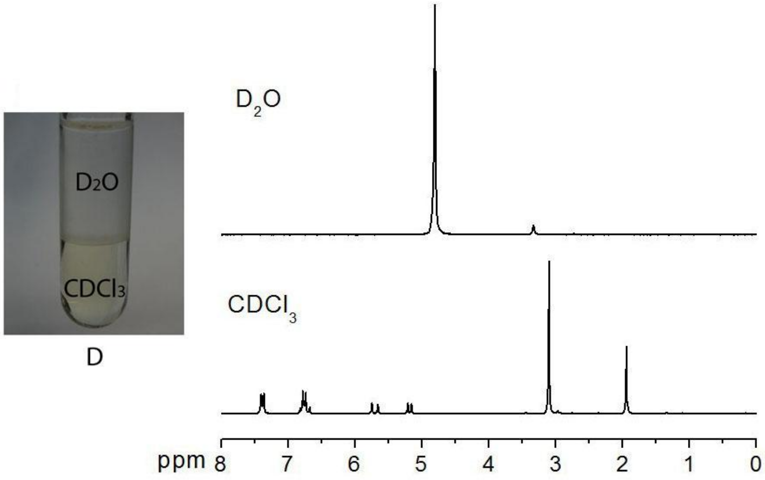


Figure 3.10: ^{1}H NMR spectra of the monomer DMVPA dissolved in the mixture of D_2O and $CDCl_3$ after N_2 bubbling

At last, N_2 was bubbled through the mixture of D_2O, MeOD and $CDCl_3$ to convert the bicarbonate salt to its natural form. MeOD evaporated during the process of N_2 bubbling. Additionally, $CDCl_3$ was thus added to maintain the same amount of the organic layer before methanol was all gone. When the liquid settled and separated into two phases again, the upper layer of the two-layer mixture was D_2O with no color and the bottom layer was $CDCl_3$ solution of the monomer with yellow color (Figure 3.6 D). The ^{1}H NMR spectra of these two layers are shown in Figure 3.10, which indicates that the colorless and clear upper layer was pure D_2O with a small amount of residual MeOD but no any monomer or its bicarbonate salt left while the yellow layer at the bottom was the $CDCl_3$ solution of the natural form of DMVPA with little residual MeOD.

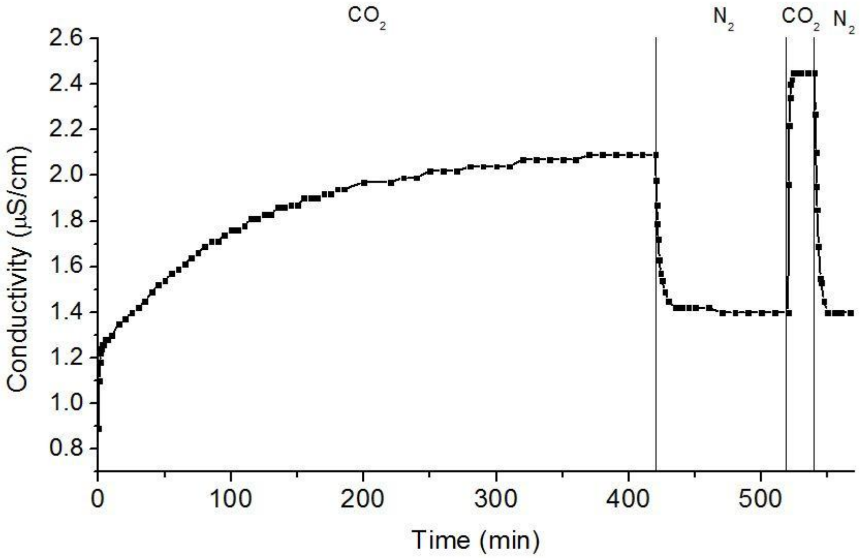


Figure 3.11: Conductivity of the monomer DMVPA in DMSO with bubbling CO_2 and N_2 alternately at 19.1 °C

To further determine the switchability of DMVPA with alternation of CO_2 and N_2 atmosphere, the conductivity of a DMSO solution of the monomer was tested. First, without stirring, the conductivity increased very slowly with CO_2 bubbling, suggesting a mass transfer limitation. To tackle this issue, a stirring bar was added to the solution and the testing vial was placed on a stirrer. In a subsequent trial, CO_2 was kept bubbling through the solution until the conductivity started to level off after 420 min as shown in Figure 3.11. The conductivity increased from about 0.9 µS/cm to 2.1 µS/cm. When N_2 was bubbled through the solution, the conductivity decreased quickly but only to 1.4 µS/cm in 100 min. When CO_2 was bubbled to the solution for a second time, the conductivity increased to 2.4 µS/cm very rapidly in 20 min. It was the same when N_2 was bubbled to the solution at the second time. The conductivity decreased very fast to the same level as in the first cycle in 20 min.

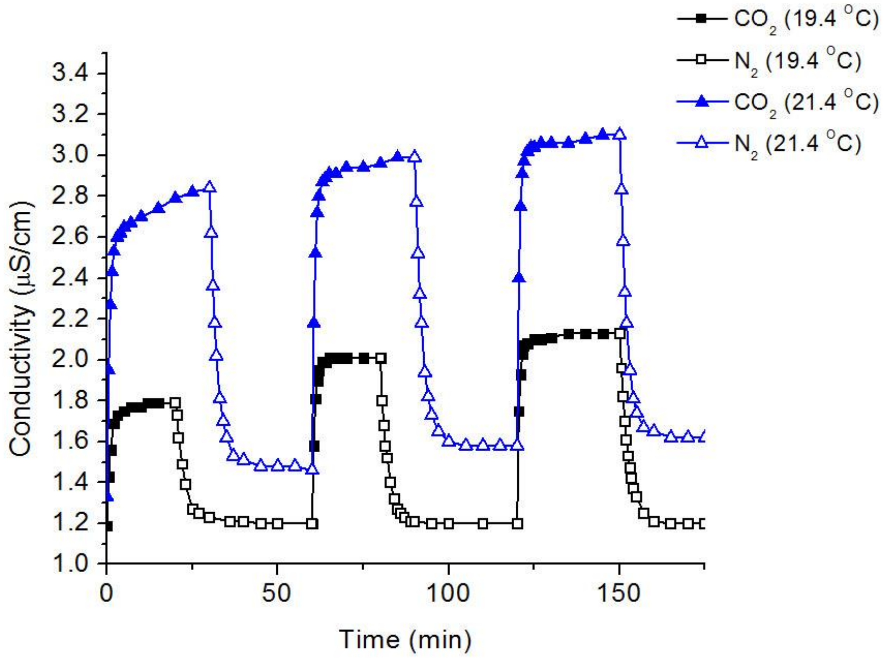


Figure 3.12: Conductivity of the monomer DMVPA in DMSO with bubbling CO_2 and N_2 alternately at different temperatures

Then different conductivity tests were carried out in shorter cycles of CO_2 and N_2 bubbling at different temperatures. The results are shown in Figure 3.12. At 19.4 °C, the conductivity increased and became levelled off after 20 min of CO_2 bubbling (at a rate of 0.2 uS/cm in 10 min) in the first cycle. The conductivity decreased to its initial value with N_2 bubbling. Bubbling CO_2 in the second cycle made the conductivity increase faster than that in the first cycle. The conductivity reached 2.0 µS/cm in 20 min, which was higher than the level-off value of the first cycle. In the third and fourth cycles, the conductivity with CO_2 bubbling increased even faster and reached a higher value. In the cycles, the conductivity decreased to the initial value with N_2 bubbling.

Temperature was found to be a very important factor in the conductivity tests. The conductivity tests of the DMSO solution with the same DMVPA concentration were carried out at 21.4 and 22.4 °C, as shown in Figure 3.14. The conductivity results of these two tests were both higher than that at 19.4 °C. The conductivity at 21.4 °C was about 0.8 µS/cm higher than that at 19.4 °C. The temperature dependence of conductivity showed the effect of temperature on the activity of the reaction between DMVPA and CO_2.

The results of the monomer partitioning test and conductivity test indicated that in each cycle of bubbling CO_2, not all the natural form monomer could be ionized by CO_2 in wet DMSO, but the reactivity of monomer increased after each cycle and so did the conductivity. On the other hand, all the ionized monomer could be deionized by N_2 bubbling and thus the conductivity decreased to its initial level.

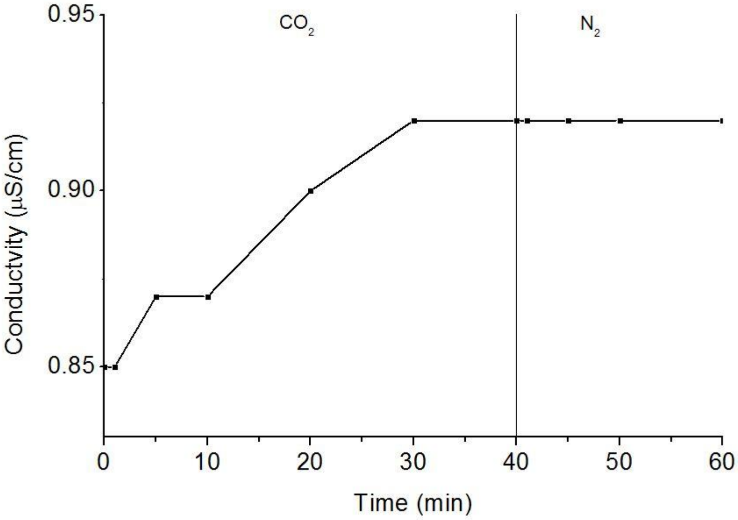


Figure 3.13: Conductivity of pure DMSO when CO_2/N_2 bubbling

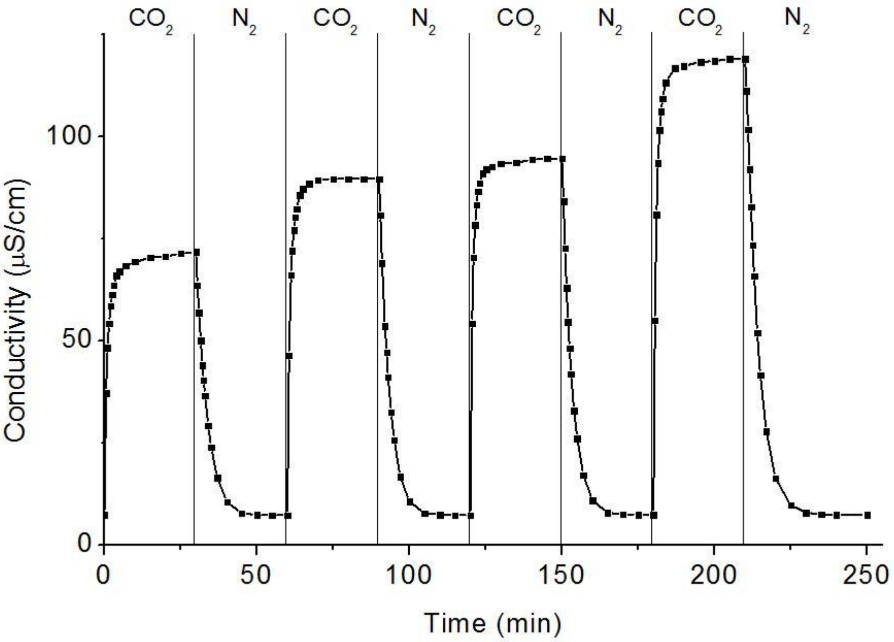


Figure 3.16: Conductivity of the monomer DMVBA in DMSO with alternate CO_2/N_2 bubbling at 19.8 °C with stirring for four cycles

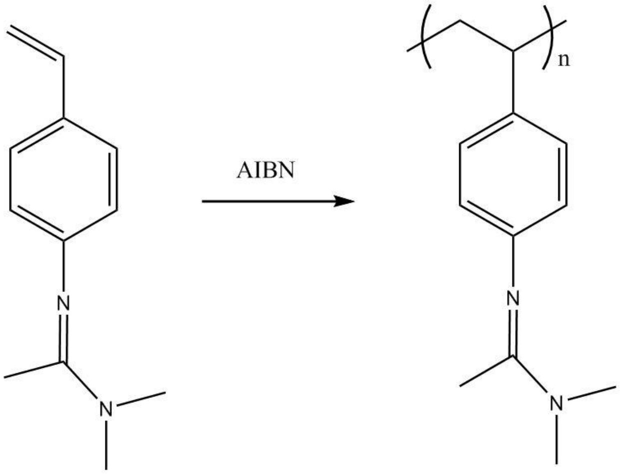
In a control test, CO_2 and N_2 were bubbled to pure DMSO in one cycle. The conductivity data were collected. In the first 40 minutes, the conductivity increased only 0.07 μS/cm by CO_2 bubbling, and it did not decrease with 20 min N_2 bubbling (Figure 3.13). This result showed that DMSO had a minor effect on the monomer conductivity in DMSO solution. Because DMSO has a very high boiling point, it volatility should not be a factor in affecting the conductivity tests.

For comparison to DMVPA, Figure 3.14 shows the conductivity test result of monomer DMVBA. Their conductivity behaviours were similar. The conductivity increased faster in each cycle with CO_2 bubbling. It decreased to its initial value with N_2 bubbling. However, the DMVBA conductivity was much higher than that of DMVPA at the same concentration (almost two orders of magnitude). The pK_a values got from the potentiometric titration of the two monomers, DMVPA and DMVBA, are about 9.7 and 10.6 respectively. The reason might be due to the conjugation between benzene ring and the amidine group in DMVPA that stabilized the charge with resonance and caused the lower conductivity of DMVPA in DMSO solution.

3.2. Switchable Polymers

3.2.1. Synthesis and Characterization of the Polymer PDMVPA

PDMVPA was synthesized by conventional free radical polymerization method using AIBN as initiator, as described in the experimental section. The structure of PDMVPA is shown in Scheme 3.4.



Scheme 3.4: Synthesis of PDMVPA

The ^{1}H NMR spectrum of PDMVPA synthesized with the DMVPA/AIBN ratio of 25:1 is shown in Figure 3.15. The signals of the protons were defined, and the integration of each peak correlated closely, with the number of protons of this polymer.

In the mass spectrum of the same polymer sample, the space between the higher peaks was about 188, confirming that the repeating unit was the monomer DMVPA. The polymer chains could be terminated by various reactions including chain transfer to monomers, to protons or to other polymer chains. So the chain ends might vary, and thus some spaces between the peaks are not exactly 188.

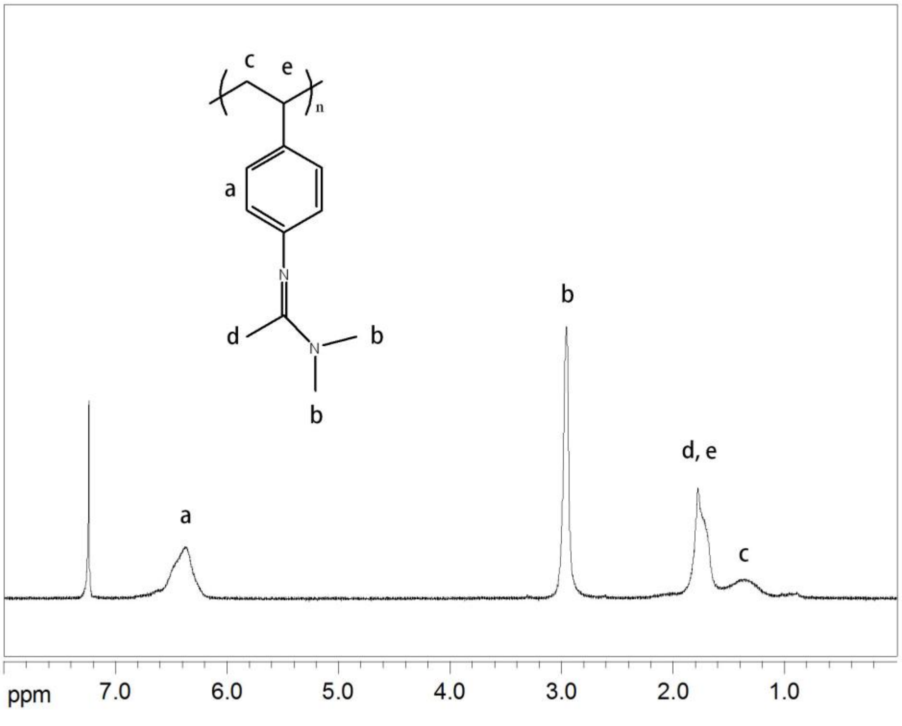


Figure 3.15: ^{1}H NMR spectrum of PDMVPA in $CDCl_3$

The FTIR spectrum of the monomer DMVPA (Figure 3.16 a) was used for comparison with that of its polymer PDMVAP (Figure 3.16 b). The signals of the hydrogen bonds, C-H stretching, C-C ring stretching, C-N stretching and o-disubstituted benzenes remained the same after polymerization. The C-C stretching around 800-1200 cm^{-1} in the spectrum of PDMVPA and the C=C stretching around 1620-1680 cm^{-1} in the spectrum of DMVPA were weak and overlapped with other stronger peaks, and thus difficult to define.

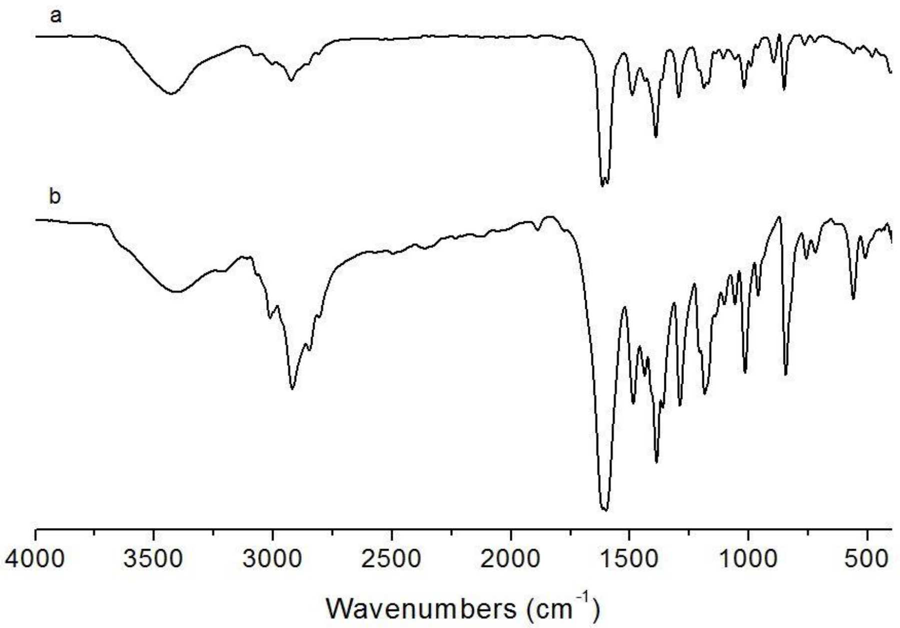
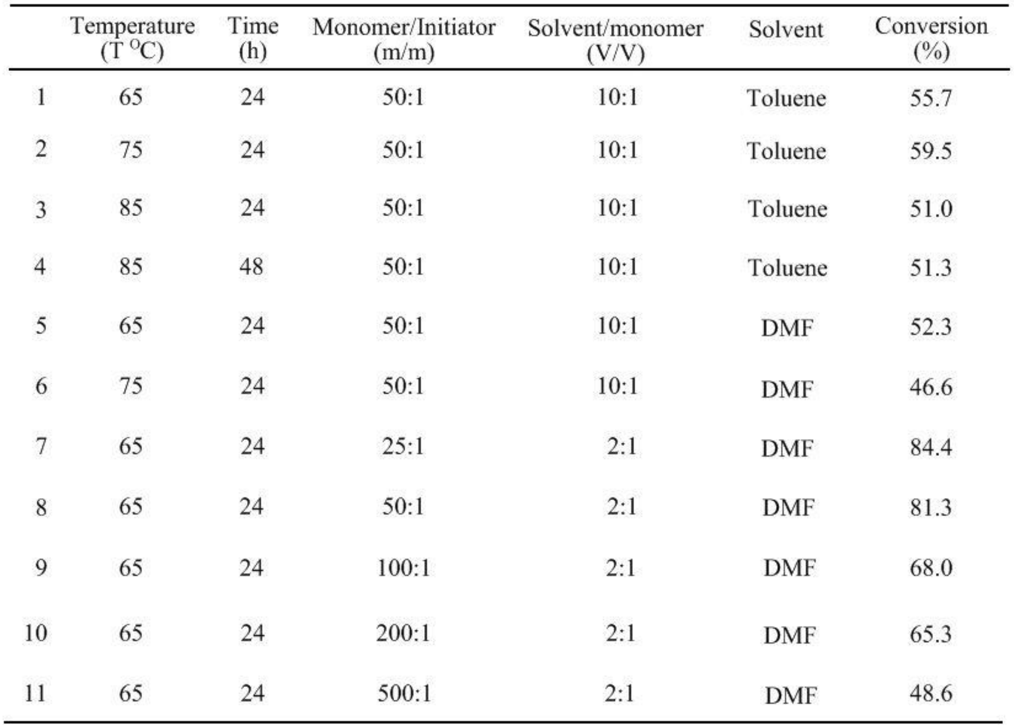


Figure 3.16: FTIR spectra of the monomer DMVPA (a) and its polymer PDMVPA (b)

Table 3.2 summarizes the polymerization conversion results at different conditions. When the polymerization was terminated by placing the tube in an ice bath, a small amount of the mixture was collected from each tube and dried in a vacuum oven to remove the solvent. The conversions were estimated from the ratios of the monomer residue and polymer peaks in the ^{1}H NMR spectra of the reaction mixtures. Toluene was used as solvent, and polymerization temperature and time varied. Increasing temperature from 65 °C to 75 °C did not increase the conversion. Further increasing temperature to 85 °C lowered the conversion. At 85 °C, increasing time from 24 hrs to 48 hrs did not increase the conversion either. The GPC curve of the polymer obtained after 48 hrs has a big tail (Figure 3.17) compared to that of 24 hrs. It suggests some coupling termination among polymer chains after 24 hrs, which caused the increase of molecular weight.

Table 3.2: Conversion of DMVPA in polymerization under various conditions



	Temperature (T ^{O}C)	Time (h)	Monomer/Initiator (m/m)	Solvent/monomer (V/V)	Solvent	Conversion (%)
1	65	24	50:1	10:1	Toluene	55.7
2	75	24	50:1	10:1	Toluene	59.5
3	85	24	50:1	10:1	Toluene	51.0
4	85	48	50:1	10:1	Toluene	51.3
5	65	24	50:1	10:1	DMF	52.3
6	75	24	50:1	10:1	DMF	46.6
7	65	24	25:1	2:1	DMF	84.4
8	65	24	50:1	2:1	DMF	81.3
9	65	24	100:1	2:1	DMF	68.0
10	65	24	200:1	2:1	DMF	65.3
11	65	24	500:1	2:1	DMF	48.6

No GPC signal was obtained with toluene as eluent, suggesting toluene was not a good solvent for PDMVPA. DMF was then chosen to used as a solvent. The polymer samples with five different monomer/initiator ratios were prepared with DMF as solvent at 65 °C for 24 hrs (Table 3.2 7-11).

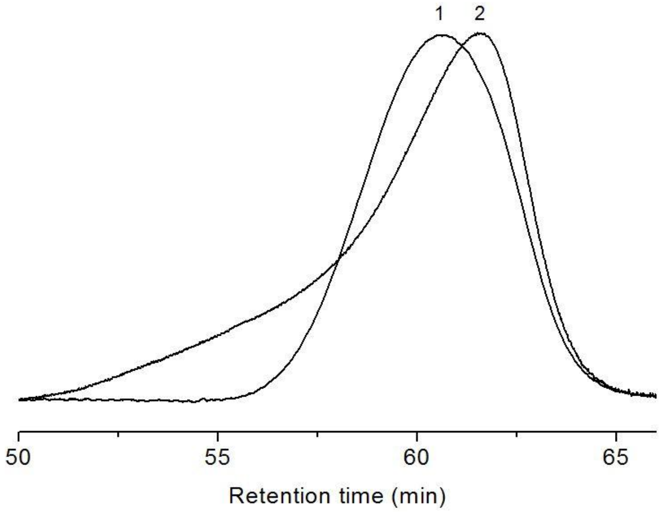


Figure 3.17: GPC curves of Entries 1 (1) and 4 (2) in Table 3.2

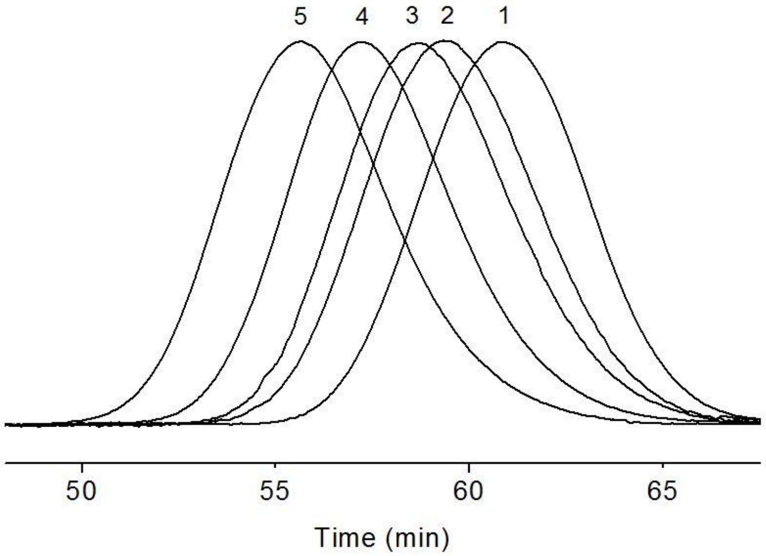
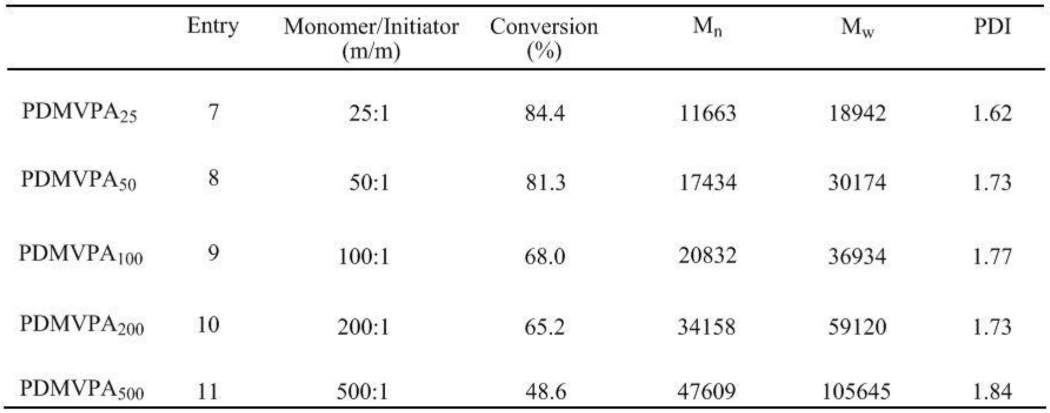


Figure 3.18: GPC curves of Entries 7-11 (1-5) in Table 3.2

Figure 3.18 shows the GPC curves of the five polymers. Increasing the monomer/initiator ratio from 25:1 to 500:1, the polymer molecular weight increased. All the five GPC curves were unimodal and symmetric.

The polymer molecular weight information is summarized in Table 3.3. $PDMVPA_{25}$ represents the polymer synthesized with 25:1 monomer/initiator ratio and so forth. The conversions decreased with the increased monomer/initiator ratio. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) all increased with the increased initiator ratio. A series of narrow polystyrene standards was used for GPC calibration. Because of the amidine groups, PDMVPA was expected to have different hydrodynamic volume than the PS standards. The absolute molecular weight data obtained by GPC only served as a reference and mainly for comparison purposes.

Table 3.3: Polymer molecular weight in Figure 3.18



	Entry	Monomer/Initiator (m/m)	Conversion (%)	M_n	M_w	PDI
$PDMVPA_{25}$	7	25:1	84.4	11663	18942	1.62
$PDMVPA_{50}$	8	50:1	81.3	17434	30174	1.73
$PDMVPA_{100}$	9	100:1	68.0	20832	36934	1.77
$PDMVPA_{200}$	10	200:1	65.2	34158	59120	1.73
$PDMVPA_{500}$	11	500:1	48.6	47609	105645	1.84

The GPC M_n of $PDMVPA_{25}$ was much higher than that of the mass spectroscopy. It was difficult for MALDI to pick up high MW polymer chains. The MALDI molecular weight and polydispersity could thus be lower than the real value.

3.2.2. Switchability of the Polymer PDMVPA

The bicarbonate salt of PDMVPA for TGA test was prepared in a similar way as that of the monomer DMVPA. $PDMVPA_{25}$ was grinded first and was stored under CO_2 atmosphere before test. A mass change of -1.4 % was observed from room temperature to about 230 °C (Figure 3.19). After that, the polymer chain started to decompose. The polymer decomposition temperature was lower than that of the monomer (300 °C). The weight loss of CO_2 and H_2O could thus be higher than 1.4 %. About 6.25 % of the total number of amidine groups was ionized by CO_2.

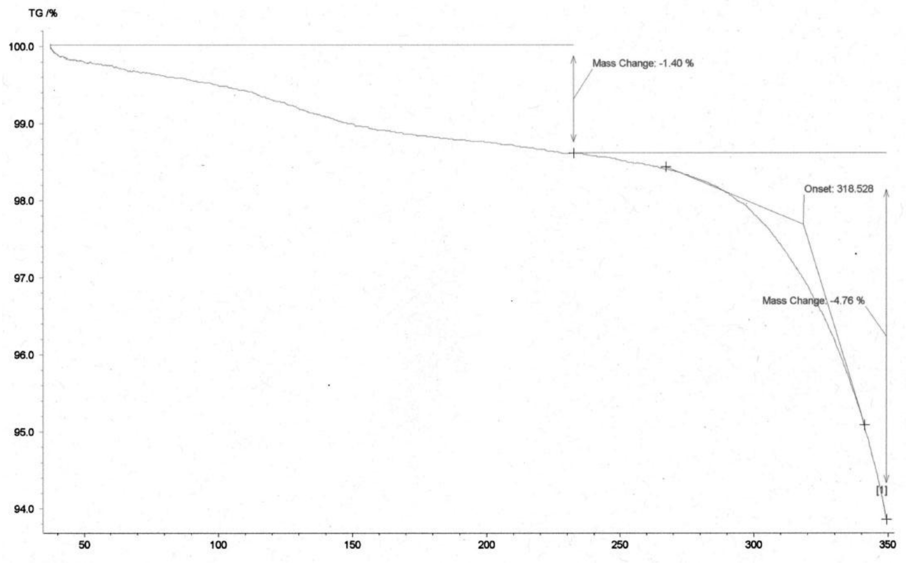


Figure 3.19: TGA trace of $PDMVPA_{25}$ after stored in CO_2

Another polymer sample was prepared in a different way for TGA test. After polymerization in DMF, CO_2 was bubbled to the reaction mixture for 1 hr. The resulted polymer was then precipitated in diethyl ether and dried. Its thermal stability was tested, but a similar result was obtained.

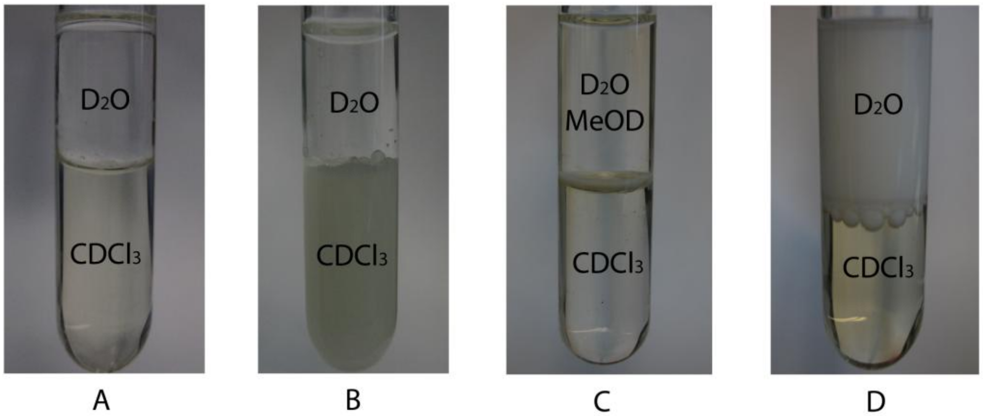


Figure 3.20: Pictures of the polymer $PDMVPA_{25}$ partitioning in D_2O and $CDCl_3$: PDMVPA in mixture of D_2O and $CDCl_3$ (A); after CO_2 bubbling (B); bicarbonate salt form of $PDMVPA_{25}$ in mixture of D_2O, MeOD and $CDCl_3$ (C) and after N_2bubbling and MeOD evaporation (D)

The partitioning of $PDMVPA_{25}$ in $CDCl_3$ and D_2O was tested, as well. First, $PDMVPA_{25}$ was dissolved in $CDCl_3$ and charged to a tube. About 1.5 mL D_2O was then added. The tube was shaken and stored in a refrigerator overnight to make the mixture settle and separate. The D_2O phase was colorless, and the $CDCl_3$ phase was yellow (Figure 3.20 A). The aqueous phase and the organic phase were collected for ^1H NMR measurements. The results are shown in Figure 3.21. $PDMVPA_{25}$ dissolved only in $CDCl_3$ but not in D_2O. The ^1H NMR spectrum of the aqueous phase was identical to the pure D_2O and so was the spectrum of the organic phase to the polymer (Figure 3.15).

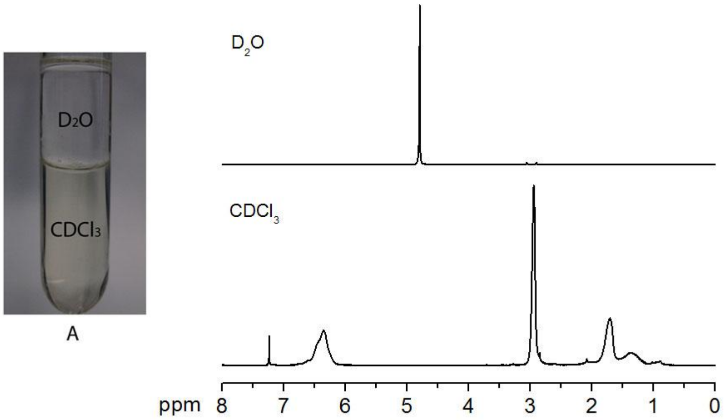


Figure 3.21: ^{1}H NMR spectra of aqueous and organic phases when the polymer PDMVPA$_{25}$ dissolved in mixture of D_2O and $CDCl_3$

After ^{1}H NMR tests, the two samples were returned to the tube, and CO_2 was bubbled through the mixture for 1 hr. Then some $CDCl_3$ was added during bubbling CO_2. The bottom layer became cloudy while the upper layer was pale yellow (Figure 3.20 B). The observation indicated that some amidine groups formed its bicarbonate salt which has low solubility soluble in $CDCl_3$. A trace amount of the bicarbonate salt might go to the upper layer and dissolve in D_2O. The aqueous layer was collected for ^{1}H NMR test. To evaporate $CDCl_3$, CO_2 was continuously bubbled into the remaining mixture. The solid residue was dissolved in MeOD and then collected to run a ^{1}H NMR test. Figure 3.22 shows the spectrum of the MeOD solution. The spectrum of the D_2O phase after CO_2 bubbling showed that there was slight amount of the bicarbonate salt of the polymer dissolved in the aqueous phase. The polymer dissolved in D_2O could be the polymer chains having a high bicarbonate salt content, while the other polymer chains dissolved much better in MeOD.

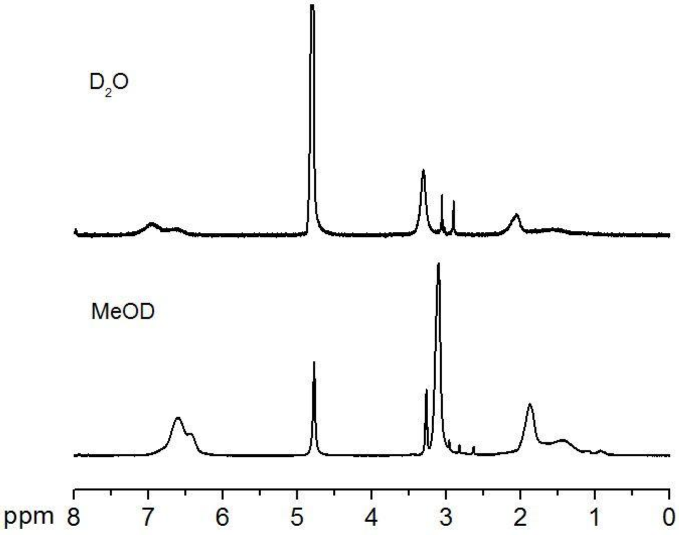


Figure 3.22: ^1H NMR spectra of bicarbonate salt form of the polymer $PDMVPA_{25}$ in D_2O and MeOD

The D_2O and MeOD solution samples were poured back to the tube, and some $CDCl_3$ was added. The upper layer was the mixture of D_2O and MeOD solutions with yellow color while the bottom layer was almost colorless $CDCl_3$ (Figure 3.20 C). N_2 was bubbled through the mixture for 1 hour. During the bubbling, MeOD was evaporated, and some $CDCl_3$ was added to keep the solution concentration. Upon phase separation, the upper aqueous layer became an emulsion with milky color and the bottom layer was $PDMVPA_{25}$ in yellow (Figure 3.20 D). The emulsion formation could be attributed to some polymer chains containing both natural form and bicarbonate salt of the amidine groups acted as an emulsifier. D_2O, $CDCl_3$ and the emulsifier were than mixed by N_2 bubbling. This was the reason that the upper layer increased in volume after MeOD evaporation. The bottom organic phase was collected to run ^1H NMR test, and the spectrum was shown in Figure 3.23. The spectrum shows that $PDMVPA_{25}$ was dissolved in $CDCl_3$ with a peak of MeOD residue. The spectrum was similar to those in Figure 3.15 and Figure 3.21.

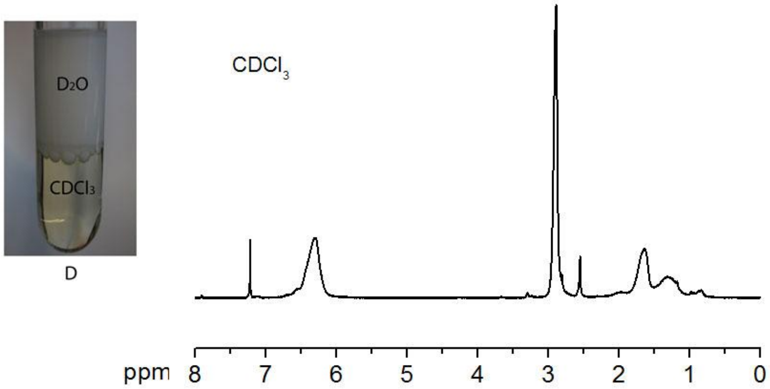


Figure 3.23: ^{1}H NMR spectra of polymer $PDMVPA_{25}$ dissolve $CDCl_3$ after bubble N_2 into the mixture of D_2O and $CDCl_3$

To further study the polymer switchability, the conductivity test of DMSO solution of $PDMVPA_{25}$ was carried out by bubbling CO_2 and N_2 alternately in shorter cycles (Figure 3.24). The result was similar to the first test of the monomer's conductivity (Figure 3.12). The conductivity also increased with CO_2 bubbling and decreased to the initial level after N_2 bubbling. In the second cycle, the conductivity increased faster and reached a higher level. Four short cycles were repeated to demonstrate the switchability of the polymer. The conductivity behaviors of the polymer and its monomer at the same concentration were very similar (both 46.6 mg in 12 mL DMSO).

Temperature was also found to be an important factor that influenced the polymer conductivity. Decreasing temperature from 22.4 °C to 19.4 °C lowered the conductivity by 0.6 µS/cm to 2.25 µS/cm in the first cycle. However, the pattern of the conductivity curve was the same at the two temperatures. The test at 21.4 °C gave the conductivity data between those of the tests at 22.4 °C and 19.4 °C (Figure 3.24).

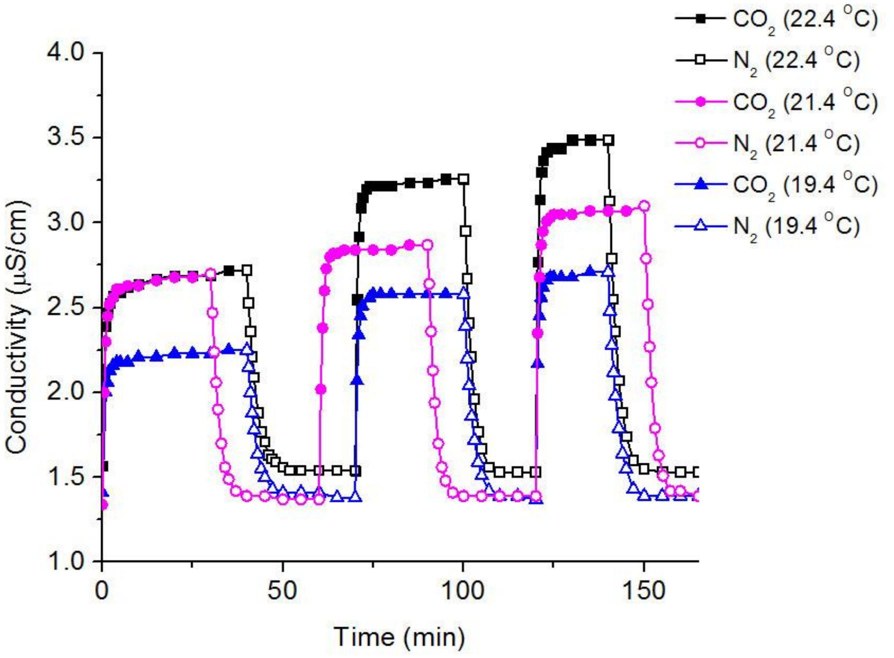


Figure 3.24: Conductivity of the polymer $PDMVPA_{25}$ in DMSO with alternate CO_2/N_2 bubbling at different temperatures

The apparent constant of degree of base protonation is a quantitative parameter of the switchability of amidine bearing polymers. The potentiometric titration was employed to further study the influence of molecular weight of polymers to the reaction of amidine functional group and CO_2. When amidine containing polymers react with CO_2 or other acids, the protonation equilibrium can be expressed as:

$$\mathrm{B+H_2O} \underset{\mathrm{K_a}}{\rightleftharpoons} \mathrm{BH^+ + OH^-}$$

Similarly to the dissociation of acids (Nagasawa 1965, Zhao 2011), the degree of protonation and the constant K_a of the amidine containing monomer DMVPA and PDMVPA polymers can be calculated according to the following equations:

$$K_a = \frac{[B][H^+]}{[BH^+]} \qquad (1)$$

$$\delta = \frac{[BH^+]}{[BH^+]+[B]} = \frac{[Acid]-[H^+]+[OH^-]}{[B]_0} \qquad (2)$$

$$pK_a = pH - \log\frac{1-\delta}{\delta} \qquad (3)$$

Figure 3.25 shows the plots of constant pK_a versus the degree of protonation (δ) for the monomer DMVPA and PDMVPA polymers with five different molecular weights, respectively. The pK_a value of monomer was higher than those of polymers and almost kept constant when δ was less than 0.8. When δ was higher than 0.8, the pK_a value decreased, it might be the reason that in the partitioning test of monomer DMVPA, some monomer residue was detected after bubbling CO_2 in the organic phase. In contrast, the pK_a values of the polymers were lower and decreased with the increasing of δ. From the result, δ was influenced by the charge density on the polymer chains. Because of an electrostatic effect, the neighbouring positively charged amidine groups attract the nearby hydroxide ions OH^-. These OH^- ions will then attract the proton cations H^+ from acids. The attraction hinders the protonation of amidine groups. So with the increasing of δ, the attraction forces increased, and as a result, the pK_a of the polymers decreased. A similar trend and a significant decrease in pK_a values were observed in all the polymers with different molecular weights. Extrapolating the pK_a vs δ curves in Figure 3.25 to $\delta = 0$ gives an initial pK_0 of about 9.5 for all of the polymers, which is closed to the pK_a of monomer PDMVPA.

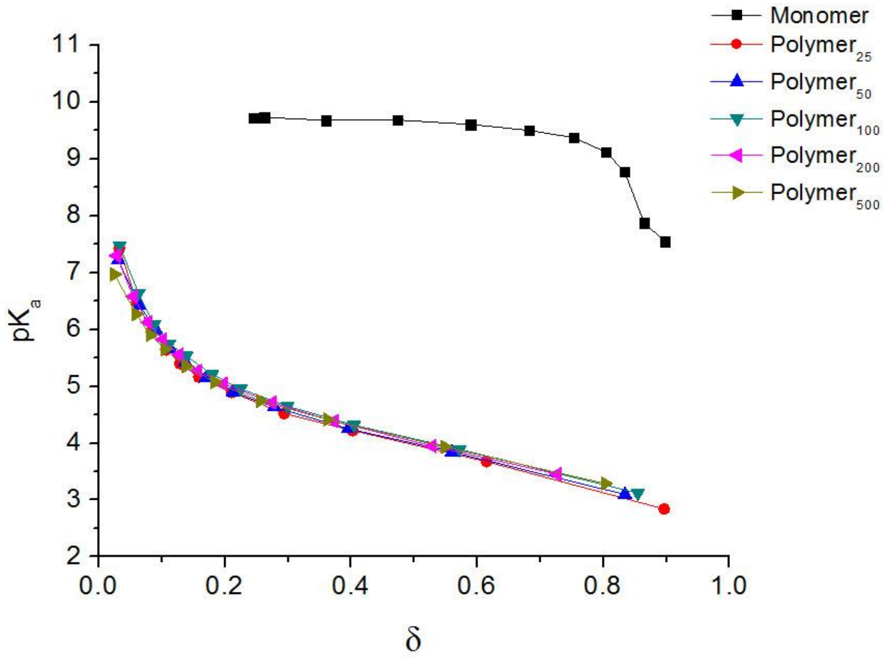


Figure 3.25: Plot of pK_a against δ for the monomer DMVPA and five PDMVPA polymers with different molecular weights

In Figure 3.26, δ values are plotted against pH of the PDMVPA polymers. The δ value changes of the polymers had the same trend. The δ values increased mildly with the pH decreasing from 6.0 to 4.5, while increased sharply with the pH decreasing from 4.5 to 3.6. It might be because that at the beginning, protonation of the amidine groups generated more neighboring positively charged groups and suppressed the protonation of amidine groups; but later the chain expansion increased their distances and balanced the attractive forces. All the δ values of the five polymers showed the similar sensitive to pH changes.

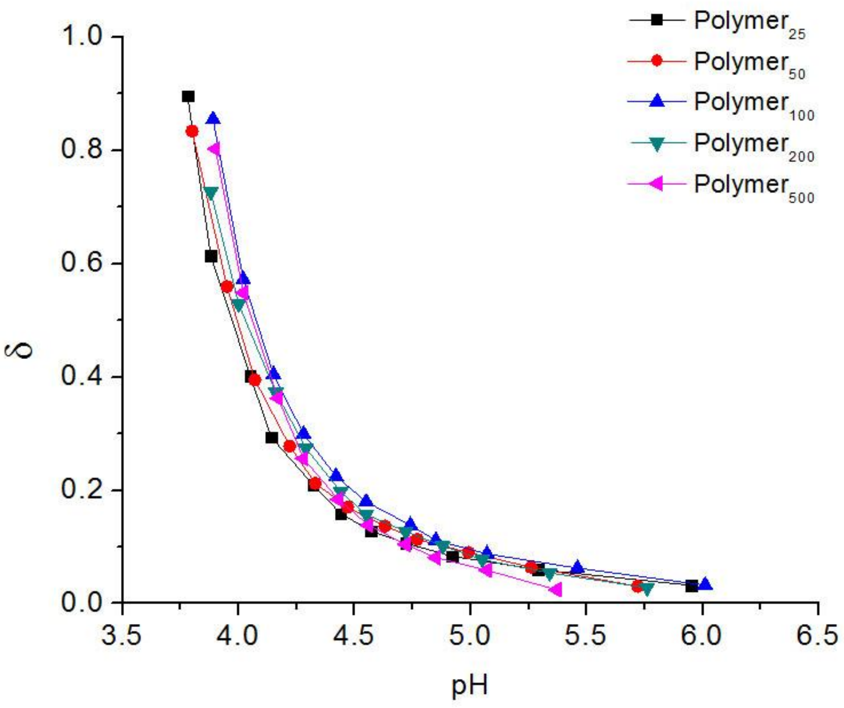


Figure 3.26: Plot of δ against pH for the PDMVPA polymers

3.3. Effect of Molecular Weight on the Polymer Switchability

The conductivity tests were carried out for all the five polymers listed in Table 3.3. Figure 3.27 shows the effects of polymer molecular weight on the conductivity of DMSO solution at the same concentration and temperature. The conductivity of $PDMVPA_{25}$ was only slightly lower than that of monomer DMVPA in each cycle of CO_2 bubbling. Because the same amount of the sample was used (46.6 mg in 12 mL DMSO), the amidine concentrations in the polymer and monomer solutions could be considered as the same.

The conductivity of the polymer solution decreased with the increased molecular weight from $PDMVPA_{25}$ to $PDMVPA_{50}$. The difference in molecular weight between $PDMVPA_{50}$ and $PDMVPA_{100}$ was not significant (see Table 3.3). The conductivity of $PDMVPA_{100}$ did not decrease much from $PDMVPA_{50}$. The initial conductivity value of $PDMVPA_{100}$ was lower than that of $PDMVPA_{50}$. It might be attributed to the poorer solubility of $PDMVPA_{100}$, which required extra heat for the mixture of polymer to dissolve in DMSO to achieve a clear solution.

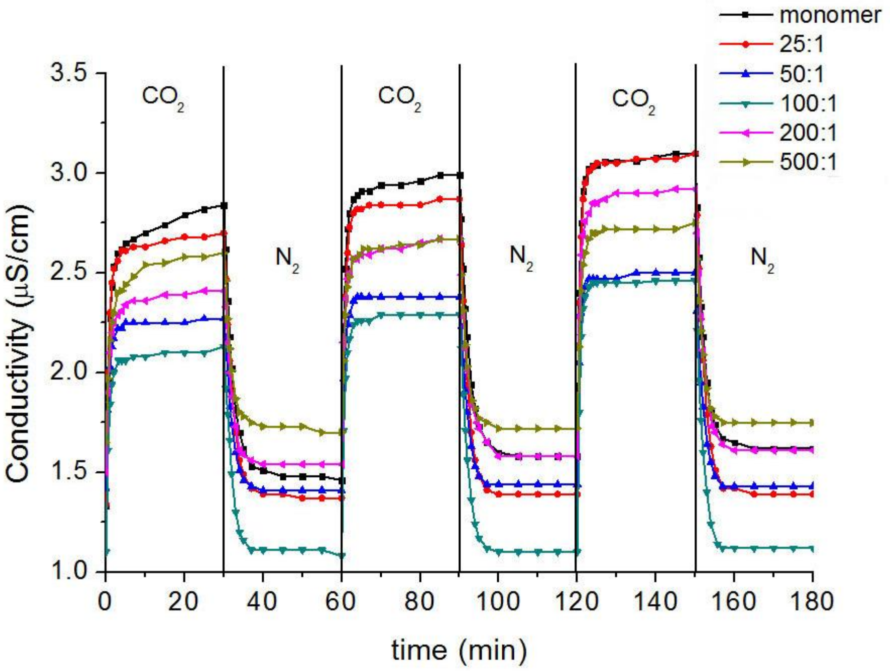


Figure 3.27: Conductivity curves of $PDMVPA_{25}$, $PDMVPA_{50}$, $PDMVPA_{100}$, $PDMVPA_{200}$ and $PDMVPA_{500}$ in DMSO with alternate CO_2/N_2 bubbling at 21.4 °C

The solubility of $PDMVPA_{200}$ and $PDMVPA_{500}$ in DMSO was even poorer. After stirred for overnight, the two solutions were still very cloudy. Heating the vials could make the solutions become clear, but the solutions became cloudy again when cooled down to room temperature. The decreased solubility with the molecular weight resulted in the abnormal results in the conductivity tests. $PDMVPA_{200}$ gave a higher conductivity than $PDMVPA_{50}$ in the first cycle of CO_2 bubbling. The conductivity of $PDMVPA_{500}$ in each cycle could increase almost to the same level. The polymer chains of $PDMVPA_{200}$ and $PDMVPA_{500}$ might be partially dissolved in DMSO and soluble portion might have shorter chains. The $PDMVPA_{200}$ and $PDMVPA_{500}$ solutions became less cloudy with CO_2 bubbling because the bicarbonate salt form of the polymers had better solubility in DMSO than the natural form polymers.

Upon CO_2 until saturation, the pH of the solutions increased from 4.228 to 4.428 with the increasing of molecular weight. It means with the same value of δ, the pK_a value of the polymers would decrease with the increasing of molecular weight. Combined with the potentiometric titration result, it could be concluded that, with higher molecular weight, the protonation of amidine groups experience more severe hinderance in the reaction of their neighbouring amidine groups with proton cations. Also with longer polymer chain length, the chain expansion became more difficult. So the polymers with lower molecular weight had the higher reactivity with acid, and as a result, the better switchability when reacted with CO_2.

CHAPTER 4

CONCLUSIONS AND RECOMMEDATIONS

4.1 Conclusions

A new type of amidine containing CO_2 responsive monomer has been designed and synthesized. A series of polymers with different molecular weights has been prepared from one monomer via conventional polymerization. The structures of the monomer and polymers have been confirmed by ^{1}NMR, MS and FTIR methods. The CO_2 switchability of the monomer and polymers were investigated by TGA, conductivity tests and potentiometric titration. The following conclusions were reached:

The monomers were synthesized in a simple one-step organic reaction which involves only two chemicals. At the same time, the crude product only needs very simple purification to give a relatively high yield. This is a cost effective way for monomer synthesis compared to the previous reports of CO_2 responsive materials. The reaction between the monomer and CO_2, as well as the reaction between the bicarbonate salt of the monomer and N_2, were proved to be reversible, which is evident from partitioning of the monomer in organic and aqueous phases and conductivity test of the monomers in DMSO.

The polymers obtained via conventional free radical polymerization were proved to be CO_2 responsive, as well. At room temperature, the amidine groups on the polymer chains reacted with CO_2 and formed the bicarbonate salt. This caused the increase in conductivity of the DMSO solution of the polymers. They could be neutralized using N_2

which cause the conductivity decrease to the same level of the natural form amidine containing polymers.

Temperature was found to be an important factor to the conductivity of the DMSO solution of both of the monomer and polymers. Molecular weight of the polymers also affected the CO_2 switchability of the polymers. The polymer with lower molecular weight showed the higher conductivity in solution. The potentiometric titration result indicates that when the degree of protonation of polymer increases, the amidine groups become difficult to react with acid. So the switchability decreases with the increasing of the molecular weight.

4.2 Recommendations and Future Work

To explore applications of the CO_2 switchable monomers, the development of the well-defined polymers by controlled/living polymerization methods is a key point. The CO_2 responsive polymers have potential applications in self-cleaning materials. If the polymerization of the monomer could be done by ATRP or other controlled polymerization, the polymer chain can be grafted from or grafted to a surface. The reversible responses of the polymer chains can make the surfaces easily cleaned by water with CO_2 bubbling, and become hydrophobic again by treating with air or N_2.

Block copolymers could be derived using a second co-monomer. Copolymers with appropriate hydrophilicity can be obtained by the copolymerization of CO_2 switchable monomer and co-monomer having desired properties. Also, multiple responsive polymeric materials can be obtained by copolymerization as well including block copolymers, random copolymers and cross-linking polymeric networks using different polymerization techniques.

Another recommendation for this project is to use this CO_2 switchable monomer in emulsion polymerization to synthesize the redispersible latex. In the partition test of the polymer, a stable emulsion was found after the polymer reacted with N_2. The partially positively charged polymer chains formed emulsion in the presence of water and chloroform. So with a proper formulation, this monomer could be an excellent candidate in this area.

REFERENCES

Abdallah D. J., Weiss R. G. Organogels and low molecular-mass organic gelators. Advanced material 2000, 12, 1237-1247

Alonso M. Reboto V., guiscardo L., Mate V., rodriguez-Cabello J. C. Novel photoresponsive p-pheylazaobenzene derivative of an elastin-like polymer with enhanced control of azobenzene content and without pH sensitiveness. Macromolecules 2001, 34, 8072-8077

Alonso M., Reboto V., Guiscardo L., San Martin A., Rodriguez-Cabello J. C. Spiropyran derivative of an elastin-like bioelastic polymer: photoresonsive molecular machine to convert sunlight into mechanical work. Macromolecules 2000, 33, 9480-9482

Amarne H., Baik C., Murphy S. K., Wang S. Steric and electronic influence on photochromic switching of N,C-chelate four-coordinate organoboron compounds. Chemistry: a European journal 2010, 16, 4750-4761

Amiya T., Hirokawa Y., Hirose Y., Li Y., Tanaka T. Reentrant phase transition of N-Isopropylacrylamide gels in mixed solvents. The journal of chemical physics 1987, 86, 2375-2379

Anker J. N., Hall W. P., Lyandres O., Shah N. C., Zhao J., Van Duyne R. P. Biosensing with plasmonic nanosensors. Nature Materials 2008, 7, 442-453

Aoki T., Kawashima M., Katono H., Sanui K., Ogata N., Okano T., Sakurai Y. Temperature-responsive interpenetrating polymer networks constructed with poly(acrylic acid) and poly(N, N-dimethylacrylamide). Macromolecules 1994, 27, 947

Arai K., Kawabata Y. Changes in the sol-gel transformation behavior of azobenzene moiety-containing methyl cellulose irradiated with UV light. Macromolecular rapid communications 1995, 16, 875-

Austad T., Milter J. In surfactants: fundamentals and applications in the petroleum industry. Schramm L. L. Ed. Cambridge univeristy press, Cambridge, 2000.

Babincona M., Leszczynska D., Sourivong P., Cicmanec P., Babinec P. Superparamagnetic gel as a novel material for electromagnetically induced hyperthermia. Journal of magnetism and magnetic materials 2001, 225, 109-112

Backman E. J. Peer reviewed: using CO_2 to produce chemical produces sustainably. Environmental science & technology 2002, 36, 347A-353A

Baik C., Hudson Z. M., Amarne H., Wang S. Enhacing the photochemical stability of N,C-chelate Boryl compounds: C-C bond formation versus C=C bond cis, trans-isomerization. Journal of the American chemistry society 2009, 131, 14549-14559

Baines F. L., Billingham N. C., Armes S. P. Synthesis and solution properties of water-soluble hydrophilic-hydorphobic block copolymers. Macromolecules 1996, 29, 3416-3420

Bajpai A. K., Bajpai J. Soni S. N. Preparation and characterization of electrically conductive composites of poly(vinyl alcohol)-g-poly(acrylic acid) hydrogels impregnated with polyaniline (pani). Express polymer letters 2008, 2, 26-39

Baker D. A., Paesler M. A., Lucovsky G., Agarwal S. C., Taylor P. C. Application of bond constraint theory to the switchable optical memory material $Ge_2Sb_2Te_5$. Physical review letters 2006, 96, 255501

Bayer C. L., Peppas N. A. Advances in recognitive, conductive and responsive delivery systems. Journal of controlled release 2008, 132, 216-221

Borgioli L., Gionannoni F., Giovannoni S. A new supportante in the frescoes sector: Carbogel. Kermes 2001, 44, 63-68

Brazel C. S., Peppas N. A. Synthesis and characterization of thermo-and chemomechanilly responsive poly(N-isopropylacrylamide-co-methacrylic acid) hydrogels. Macromolecules 1995, 28, 8016-8020

Brownlee M., Cerami A. A glucose-controlled insulin-delivery system: semisythetic insulin bound to lectin. Science 1979, 206, 1190-1191

Canevet D., Salle M., Zhang G., Zhang D., Zhu D. Tetrathiafulvalene (TTF) derivatives: key building-blocks for switchable processes. Chemical communications 2009, 2245-2269

Caretti E., Bonini M., Dei L., Berrie B. H., Angelova L. V., Baglioni P., Weiss R. G. New frontiers in materials science for art conservation: responsive gels and beyond, Accounts of chemical research, 2010, 43, 751-760

Carretti E., Dei L., Baglioni P. solubilization of acrylic and vinyl polymers in nanocontainer solutions. Application of microemulsions and micelles to cultural heritage conservation. Langmuir 2003, 19, 7867-7872

Carretti E., Dei L., Baglioni P., Weiss R. G. Synthesis and charaterization of gels from polyallyamine and carbon dioxide as gellant. Journal of the American Chemical Society 2003, 125, 5121-5129

Carretti E., Dei L., Weiss R. G. Soft matter and art conservation: rheoreversible gels and beyond. Soft matter 2005, 1, 17-22

Carretti E., Dei L., Weiss R. G., Baglioni P. A new class of gels for the consevation of painted surfaces. Journal of cultural heritage 2008, 9, 386-393

Carretti E., Fratini E., Berti D., Dei L., Baglioni P. Nanoscience for art conseration: o/w microemulsions embedded in a polymeric network for the cleaning of works of art. Angewandte Chemie International Edition, 2009, 48, 8966-8969

Carretti E., Giorgi R., Berti D., Baglioni P. Oil-in-water nanocontainers as low environmental impact cleaning tools for works of art: Two case studies. Langmuir 2007, 23, 6396-6403

Carretti E., Grassi S., Cossalter M., Natali I., Caminati G., Weiss R. G., Baglioni P., Dei L. Poly(vinyl alcohol)-borax hydro/coscolvent gels. Viscoelastic properties, solubilizing power, and application to art conservation. Langmuir 2009, 25, 8656-8662

Chen G., Hoffman A. S. Graft copolymers that exhibit temperature-induced phase transitions over a wide range of pH. Nature 1995, 373, 49-52

Cremonesi P., Curti A., Fallarini L., Raio S. Preparation and use of solvent gels, reagents for the cleaning of polychrome works. Progetto Restauro 2000, 7, 25-33

Da Silveira L. A note on the poultice cleaning of feathers using Laponite RD gel. Studies in conservation. Draguignan-Flganieres, France, 27-29 May 1998; Pennec S., Robbiola L., Eds.; James&James: London, 1998

Dai S., Ravi P., Tam K. C. pH-Responsive polymers: synthesis, properties and applications. Soft matter 2008, 4, 435-449

Dai S., Ravi P., Tam K. C. Thermo- and photo-responsive polymeric systems. Soft Matter 2009, 5, 2513-2533

Dai S., Tam K. C. Jenkins R. D. Dissolution behavior of HASE polymers in the presence of salt: potentiometric titration, isothermal titration calorimetry, and light scattering studies. Journal of physical chemistry B 2002, 106, 1195-1204

Dai S., Tam K. C. Jenkins R. D. Light scattering of hydrophobically modified alkali-soluble emulsion (HASE) polymer: Ionic strength and temperature effects. Macromolecular chemistry and physics 2001, 202, 335-342

Dai S., Tam K. C. Jenkins R. D., Tan C. B. Interactions between methyacrylic acid/ethyl acrylate copolymers and dodecyltrimethylammonium bromide. Journal of physical chemistry B 2003, 107, 4667-4675

Dai S., Tam K. C. Microstructure of un-neutralized hydrophobically modified alkali-soluble emulsion latex in different surfactant solutions. Langmuir 2005, 21, 7136-7142

Dai S., Tam K. C., Jenkins R. D. Microstructure of dilute hydrophobically modified alkali soluble emulsion in aqueous salt solution. Macromolecules 2000, 33, 404-411

Dai S., Tam K. C., Jenkins R. D., Bassett D. R. Light scattering of dilute hydrophobically modified alkali-soluble emulsion solutions: effects of hydrophobicity and spacer length of macromonomer. Macromolecules 2000, 33, 7021-7028

Das M., Sanson N., Fava D., Kumacheva E. Microgels loaded with gold nanorods: photothermally triggered volume transitions under physiological conditions. *Langmuir* 2007, **23**, 196-201

De Wolfe R. H., Farnoux C. C., Fodor G., Garner L. A., Gautier J. A., Grambal F., Grout R. J., Jafelinger G., Lund H., McCarty C. G., Miocque M., Neilson D. G., Phillips B. A., Prichard W. H., Sevcik J., Shaw R., Watson K. M. The chemistry of amidines and imidates. Ed Patai S. John Wiley & Sons Ltd, 1975

Delair J. A., Nakatani K. Linear and nonlinear optical properties of photochromic molecules and materials. Chemical reviews 2000, 100, 1817-1845

Deng Y., Li N., He Y., Wang X. Hybrid colloids composed of two amphiphilic azo polymers: fabrication, characterization, and photoresponsive properties. Macromolecules 2007, 40, 6669-6678

Desponds A., Freitag R. Synthesis and charactrerization of photoresponsive n-isopropylacrylamide cotelomers. Langmuir 2003, 19, 621-6270

Desset S. L., Cole-Hamilton D. J. Carbon dioxide induced phase switching for homogeneous-catalyst recycling. Angewandte chemie international edition 2009, 48, 1472-1474

Edahiro J., Sumaru K., Tada Y., Ohi K., Takagi T., Kameda M., Shinbo T., Kanamori T., Yoshimi Y. In situ control of cell adhesion using photoresponsive culture surface. Biomacromolecules, 2005, 6, 970-974

El-Hag Ali A., Abd El-Rehim H. A., Hegazy E. S. A., Ghobashy M. M. Synthesis and electrical resonse of acrylic acid/vinyl sulfonic acid hydrogels prepared by g-irradiation. Radiation physics and chemistry 2006, 75, 1041-1046

Feng X., Zhai J., Jiang L. The fabrication and switchable superhydrophobicity of TiO_2 nanorod films. Angewandte chemie international edition 2005, 44, 5115-5118

Feringa B. L., Jager W. F., de Lange B. Organic materials for reversible optical data storage. Tetrahedron 1993, 49, 8267-8310

Filipcsei G., Feher J., Zrinyi M. Electric field sensitiveneutral polymer gels. Journal of molecular structure 2000, 554, 109-117

Fowler C. I., Muchemu C. M., Miller R. E., Phan L., O'Neill C., Jessop P. G., Cunningham M. F. Emulsion polymerization of styrene and methyl methacrylate using cationic switchable surfactants. Macromolecules 2011, 44, 2501-2509

Fujishima A., Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972, 238, 37-38

Gaudry J. B., Capes L., Langot P., Marcen S., Kollmannsberger M., Lavastre O., Freysz E., Letard J. F., Kahn O. Second-order non-linear optical response of metallo-organic compounds: towards switchable materials. Chemical physics letters 2000, 324, 321-329

George M., Weiss R. G. Molecular organogels. Soft matter comprised of low molecular-mass organic gelators and organic liquids. Accounts of chemical research 2006, 39, 489-497

Gil E. S., Hudson S. M. Stimuli-responsive polymers and their bioconjugateds. Progress in polymer science 2004, 29, 1173-1222

Goodvin A. P., Mynar J. L., Ma Y., Fleming G. R., Frechet J. M. J. Synthetic micelle sensitive to IR light via a two-photo process. Journal of the American chemistry society 2005, 127, 9952-9953

Grabe M., Oster G. Regulation of organelle acidity. The journal of general physiology 2001, 117, 329-344

Guo L., Tam K. C., Jenkins R. D. Effects of salt on the intrinsic viscosity of model alkali-soluble associative polymers. Macromolecular chemistry and physics 1998, 199, 1175-1184

Guo Z., Feng Y., Wang Y., Wang J., Wu Y., Zhang Y. A novel smart polymer responsive to CO_2. Chemical communications 2011, 47, 9348-9350

Harjani, J. R., Liang C., Jessop P. G. A synthesis of acetamidines. The journal of organic chemistry 2011, 76, 1683-1691

Heskins M., Guillet J. E. Solution properties of poly(N-isopropylacrylamide). Journal of Macromolecular science: part A - Chemistry, 1968, 2, 1441-1455

Higuchi A., Hamamura A., Shindo Y., Kitamura H., Yoon B. O., Mori T., Uyama T., Umezawa A. Photo-modulated changes of cell attachments on poly(spiropyran-co-methyl methacrylate) membranes. Biomacromolecules 2004, 5, 1770-1774

Hirokawa Y., Jinnai H., Nishikawa Y., Okamoto T., Hashimoto T. Direct observation of internal structures in poly(N-isopropylacrylamide) chemical gels. Macromolecules 1999, 32, 7093-7099

Hirokawa Y., Tanaka T. Volume phase transition in a nonionic gel. The journal of chemical physics 1984, 81, 6379-6380

Hoffman A. S. the orgins and evolution of "controlled" drug delivery systems. Journal of controlled release 2008, 132, 153-163

Homma M., Seida Y., Nakano Y. Design and optimization of high-performance electrically-driven polymer hydrogel systems. Journal of applied polymer science 2000, 75, 111-118

Horne R., Almeida J. P., Day A. F., Yu N. Macromolecule hydration and effect of solutes on the cloud point of aqueous solutions of polyvinyl methyl ether: a possible model for protein denaturation and temperature control in homeothermic animals. Journals of colloid and interface science 1971, 35, 77-84

Idziak I., Avoce D, Lessard D., Gravel D., Zhu X. X. Thermosensitivity of aqueous solutions of poly (N, N-diethylacrylamide) Macromolecules 1999, 32, 1260-1263

Ionov L., Houbenov N., Sidorenko a., Stamm M., Minko S. Stimuli-responsive command polymer surface for generation of protein gradients. Biointerphases 2009, 4, FA45-FA49

Irie M. Stimuli-responsive poly(N-isopropylacrylamide). Photo- and chemical-induced phase transitions. Advances in polymer science 1993, 110, 49-65

Irvin D. J., Goods S. H., Whinnery L. L. Direct measurement of extension and force in conductive polymer gel actuators. Chemistry of Materials 2001, 13, 1143-1145

Irvin D. J., Goods S. H., Whinnery L. L. Direct measurement of extension and force in a conductive polymer gel actuator. Chemistry of materials 2001, 13, 1143-1145

Ishikawa T., Margetic D., Kumamoto T., Kondo Y., Kotsuki H., Nagasawa K., Nakanishi W., Kumamoto T. Superbases for organic synthesis. Ed Ishikawa T. John Wiley & Sons Ltd, 2009

Ito Y., Casolaro M., Kono K., Imanishi Y. An insulin-releasing system that is responsive to glucose. Journal of controlled release 1989, 10, 195-203

Ivanov A. E., Eremeev N. L., Wahlund P. O., Galaev I. Y., Mattiasson B. Photosensitive copolymer of n-isopropylacrylamide and methacryloyl derivative of spirobenzopyran. Polymer 2002, 43, 3819-3823

Jakubiak R., Bunning T. J., Vaia R. A., Natarajan L. V., Tondiglia V. P. Electrically switchable, one-dimensional polymeric resonators form holographic photopolymerization: a new approach for active photonic bandgap matrerials. Advanced materials 2003, 15, 241-244

Jensen M., Birch Hansen P., Murdan S., Frokjaer S., florence A. T. Loading into and electro-stimulated release of peptides and proteins from chondroitin 4-sulphate hydrogels. European journal of pharmaceutical sciences 2002, 15, 139-148

Jeong B., Gutowska A. Lessons from nature: stimuli-responsive polymers and their biomedical applications. Trends in biotechnology 2002, 20, 305-311

Jessop P. G., Heldebrant D. J., Li X. W., Eckert C. A., Liotta C. L. Green chemistry-reversible nonpolar-to-polar solvent. Nature 2005, 436, 641

Jessop P. G., Phan L., Carrier A., Robinson S., Durr C. J., Harijani J. R. A solvent having switchable hydrophilicity. Green chemistry 2010, 12, 809-814

Jessop P. G., Subramaniam B. Gas-expanded liquids. Chemical reviews 2007, 107, 2666-2694

Jhaveri S. J., Hynd M. R., Dowell Mesfin N., Turner J. N., Shain W., Ober C. K. Release of nerve growth factor from HEMA hydrogel-coated substrates and its effect on the differentiation of neural cells. Biomacromolecules 2009, 10, 174-183

Jochum F. D., Theato P. Temperature and light sensitive copolymers containing azobenzene moieties prepared via a polymer analogous reaction. Polymer 2009, 50, 3079-3085

Khoukh S., Oda R., Labrot T., Perrin P., Tribet C. Light-responsive hydrophobic association of azobenzene-modified poly(acrylic acid) with neutral srufactants. Langmuir 2007, 23, 94-104

Kim S. J., Kim H. I., Shin S. R., Kim S. I. Electrical vehavior of chitosan and poly(hydroxyethyl methacrylate) hydrogel in the contract system. Journal of applied polymer science 2004, 92, 915-919

Kim S. J., Park S. J., Kim I. Y., Shin M. S., Kim S. I. Electric stimuli responses to poly(vinyl alcohol)/chitosan interpenetrating polymer network hydrogel in NaCl solutions. Journal of applied polymer science 2002, 86, 2285-2289

Kim S. J., Park S. J., Lee S. M., Lee Y. M., Kim H. C., Kim S. I. Electroactive characteristics of interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(n-isopropylacrylamide). Journal of applied polymer science 2003, 89, 890-894

Kim S. J., Park S. J., shin M. S., Kim S. I. Characteristics of electrical responsive chitosan/polyallylamine interpenetrating polymer network hydrogel. Journal of applied polymer science 2002, 86, 2290-2295

Kim S. J., shin S. R., Lee J. H., Lee Sl H., Kim S. I. Electrical response characterization of chitosan/polyacrylonitrile hydrogel in NaCl solutions. Journal of applied polymer science 2003, 90, 91-96

Kim S. J., Shin S. R., Lee S. M., Kim I. Y., Kim S. I. Electromechanical properties of hydrogels based on chitosan and poly(hydroxyethyl methacrylate) in NaCl solution. Smart materials and structures 2004, 13, 1036-1039

Kim S. J., Yoon S. G., Lee S. M., Lee S. H., Kim S. I. Electric sensitivity behavior of a hydrogel composed of poly(methacrylic acid)/poly(vinyl alcohol). Journal of applied polymer science 2004, 91, 3613-3617

Kim S. J., Yoon S. G., Lee Y. M., Kim S. I. Bending behavior of hydrogels composed of poly(methacrylic acid) and alginate by electrical stimulus. Polymer international 2004, 53, 1456-1460

Kim S. J., Yoon S. G., Lee Y. M., Kim S. I. Electrical sensitive behavior of poly(vinyl alcohol)/poly(diallyldimethylammonium chloride) IPN hydrogel. Sensors and actuators B: chemical 2003, 88, 286-291

Kim S. Y., Shin H. S., Lee Y. M., Jeong C. N. Properities of electroresponsive poly(vinyl alcohol)/poly(acrylic acid) ipn hydrogels under an electrics stimulus. Journal of applied polymer science 1999, 73, 1675-1683

Kippelen B, Marder S. R., Hendrickx E., Maldonado J. L., Guillemet G., Volodin, B. L., Steele D. D., Enami Y., Sandalphon, Yao Y. J., Wang J. F., Rockel H., Erskine L., Peyghambarian N. Infrared photorefractive polymers and their applications for imaging. Science 1998, 279, 54-57

Konak C. Rathi R. C., Kopeckova P., Kopecek J. Photoregulated association of water-soluble copolymers with spirobenzopyran-containing side chains. Macromolecules 1997, 30, 5553-5556

Kost J., Langer R. Responsive polymer systems for controlled delivery of therapeutics. Trends in biotechnology 1992, 10, 127-131

Kown Y. M., Kim S. W. Thermosensitive biodegradable hydrogels for the delivery of therapeutic agents, in: Polymeric drug delivery systems. Kwon G. S. (Ed), Taylor & Francis, Boca Raton, 2005, p251-274

Kulkarni R. V., Biswanath S. Electrically responsive smart hydrogels in drug delivery: a review. Journal of applied biomaterials & biomechanics 2007, 5, 129-139

Kumar G. S., Neckers D. C. Photochemistry of azobenzene-containing polymers. Chemical reviews 1989, 89, 1915-1925

Laloyaux X., Fautre E., Blin T., Purohit V., Leprince J., Jouenne T., Jonas A. M., Glinel K. Temperature-responsive polymer brushes switching from bactericidal to cell-repellent. *Advanced materials* 2010, **22**, 5024-5028

Lampert C. M. Chromogenic smart materials. Materials today 2004, March, 28-35

Leclerc E., Furukawa K. S., Miyata F., Sakai Y., Ushida T., Fujii T. Fabrication of microstructures in photosensitive viodegradable polymers for tissue engineering applications. Biomaterials 2004, 25, 4683-4690

Lee H. I., Pietrasik J., Matyjaszewski K. Phototunable temperature-responsive molecular brushes prepared by ATRP. Macromolecules 2006, 39, 3914-3920

Lee H. I., Wu W., Oh J. K., Mueller L., Sherwood G. Peteanu L. Kowalewski T., Matyjaszewski K. Light-induced reversible formation of polymeric micelles. Angewandte chemie international edition 2007, 46, 2453-2457

Lee J., Macosko C. W., Urry D. W. Swelling behavior of γ irradiation cross-linked elastometric polypentapeptide-based hydrogels. Macromolecules 2001, 34, 4114-4123

Lee M. J., Jung D. H., Han Y. K. Photoresponsive polymers and their applications to optical memory. Molecular crystals & liquid crystals 2006, 444, 41-50

Lekin K., Winter S. M., Downie L. E., Bao X., Tse J. S., Desgreniers S., Secco R. A., Dube P. A., Oakley R. T. Hysteretic spin crossover between a bisdithiazolyl radical and its hypervalent σ-dimer. Journal of the American chemistry society 2010, 132, 16212-16224

Lentacker I., De Geest B. G., Nandenbroucke R. E., Peeters L., Demeester J., De Smedt S. C., Sanders N. N. Ultrasound-reponsive polymer-coated microbubbles that bind and protect DNA. Langmuir 2006, 22, 7273-7278

Li C. J., Chan T. H. Organic reactions in aqueous media. Wiley: New York, 1997

Li Y., Deng Y., Tong X., Wang X. Formation of photoresponsive uniform colloidal spheres from an amphiphilic azobenzene-containing random copolymer. Macromolecules 2006, 8809, 1108-1115

Li Y., He Y., Tong X., Wang X. Photoinduced deformation of amphiphilic azo polymer colloidal spheres. The journal of American Chemistry Society 2005, 127, 2402-2403

Lin S. B., Yuan C. H., Ke A. R., Quan Z. L. Electrical response characterization of PVA-p(AA/AMPS) IPN hydrogels in aqueous Na_2SO_4 solution. Sensors and Actuators B 2008, 134, 281-286

Linsebigler A. L., Lu G., Yates J. T. Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. Chemical reviews 1995, 95, 735-758

Liu Y. X., Jessop P. G., Switchable surfactants. Science 2006, 313, 958-960

Liu Z. S., Calvert P. Multilayer hydrogels as muscle-like actuators. Advanced materials 2000, 12, 288-291

Lu Z., Kopeckova P., Kopecek J. Antigen responsive hydrogels based on polymerizable antibody fab fragment. Macromolecular bioscience 2003, 3, 296-300

Luzinov I., Minko S., Tsukruk V. V. Responsive brush layers: from tailored gradients to reversibly assembled nanoparticles. Soft Matter 2008, 4, 714-725

Makhaeva E. E., Tenhu H., Khokhlov A. R. conformational changes of poly(vinylcaprolactam) macromolecules and their complexes with ionic surfactants in aqueous solution. Macromolecules 1998, 31, 6112-6118

Marmottant P., Hilgenfeldt S. Controlled vesicle deformation and lysis by single oscillating bubbles. Nature 2003, 423, 153

Masliyah J., Zhou Z., Xu Z., Czarnecki J., Hamza H. Understanding water-based bitumen extraction from athabasca oil sands. Canadian journal of chemical engineering 2004, 82, 628-654

Matejka L., Ilusek K., Wichterle O. Photomechanical effects in crosslinked photochromic polymers. Polymer 1981, 22, 1511-1515

Mendes P. M. Stimuli-responsive surfaces for bio-applications. Chemical society reviews 2008, 37, 2512-2529

Mercer S. M., Jessop P. G. "Switchable water": aqueous solutions of switchable ionic strength. ChemSusChem 2010, 3, 467-470

Meyer V., Pilliez J., Habas J. P., Montel F., Creux P. Rheological evidence of the diffusionnal affregation of asphaltenes in extra-heavy crude oil. Energy & Fuels 2008, 22, 3154-3159

Miyata T., Asami N., Uragami T. A reversibly aitigen-responsive hydrogel. Nature 1999, 399, 766-769

Miyata T., Asami N., Uragami T. Preparation of an antigen-sensitive hydrogel using antigen-antibody bindings. Macromolecules 1999, 32, 2082-2084

Miyata T., Uragami T., Nakamae K. Biomolecule-sensitive hydrogels. Advanced drug delivery reviews 2002, 54, 79-98

Moerkerke R., Meeussen F., Koningsveld R., Berghmans H., Mondelaers W., Schacht E., Dusek K., Solc K. Phase transitions in swollen networks. 3. Swelling behavior of radiation cross-linked poly(vinyl methyl ether) in water. Macromolecules 1998, 31, 2223-2229

Moniruzzaman M., Sabey C. J., Fernando G. F. Photoresponsive polymers: an investigation of their photoinduced temperature changes during photoviscosity measurements. Polymer 2007, 48, 255-263

Motornov M., Minko S., Eichhorn K. J., Nitschke M., Simon F., Stamm M. Reversible tuning of wetting behaviour of polymer surface with responsive polymer brushes. Langmuir 2003, 19, 8077-8085

Mu L., Liu Y., Cai S. Y., Kong J. L. smart surface in a microfluidic chip for controlled protein separation. Chemistry - a European journal 2007, 13, 5113-5120

Nagai D., Suzuki A., Maki Y., Takeno H. Reversible chain association/dissociation via a CO_2 responsive crosslinking/decrosslinking system. Chemical communications 2011, 47, 8856-8858

Nagasaki T. Photoresponsive polymeric materials for drug delivery systerms: double targeting with photoresponsive polymers. Drug delivery systems 2008, 23, 637-643

Nagasawa M., Murase T., Kondo K. Potentiometric titration of stereoregular polyelectrolytes. Journal of physical chemistry 1965, 69, 4005-4012

Nagase K., Kobayashi J., Kikuchi A., Akiyama Y., Kanazawa H., Okano T. Effects of graft densities and chain lengths on separation of bioactive compounds by nanolayered thermoresponsive polymer brush surface. Langmuir 2008, 24, 511-517

Nakanishi J., Kikuchi Y., Inoue S. Yamaguchi K., Takarada T., Maeda M. Spatiotemporal control of migration of single cells on a photoactivatable cell microarray. Journal of the American chemistry society 2007, 129, 6694-6695

Nakanishi J., Kikuchi Y., Takarada T., Nakayama H., Yamaguchi K., Maeda M. Photoactivation of a substrate for cell adhesion under standard fluorescence microscopes. Journal of the American chemistry society 2004, 126, 16314-16315

Natansohn A., Rochon P. Photoinduced motions in azo-containing polymers. Chemical reviews 2002, 102, 4139-4175

o8. Heldebrant D. J., Koech P. K., Ang M. T. C., Liang C., Rainbolt J. E., Yonker C. R., Jessop P. G. Reversible zwitterionic liquids, the reaction of alkanol guanidines, alkanol amidines, and diamines with CO_2. Green Chemistry 2010, 12, 713-721

Oh J. K., Siegwart D. J., Lee H. I., Sherwood G., Peteanu I., Hollinger J. O., Kataoka K., Matyjaszewski K., Biodegradable nanogels prepared by atom transfer radical polymerization as potential drug delivery carriers: synthesis, biodegradation, in vitro release, and bioconjugation. Journal of the American chemistry society 2007, 129, 5939-5945

O'Regan B., Gratzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 film. Nature 1991, 353, 737-740

Osada Y., Okuzaki H., Hori H. A polymer gel with electrically driven motility. Nature 1992, 355, 242-243

Pal S. K., Bag P., Sarkar A., Chi X., Itkis M. E., Tham F. S., Donnadieu B., Haddon R. C. Hysteretic spin and charge delocalization in a phenalenyl-based molecular conductor. Journal of the American chemistry society 2010, 132, 17258-17264

Park K. Controlled drug delivery: challenges and strategies. ACS professional reference book, American Chemical Society: Washington, D. C., 1997

Pelton R. H., Chibante P. Preparation of aqueous latices with N-Isopropylacrylamide. Colloids and surfaces, 1986, 20, 247-256

Phan L., Anderatta J. R., Horvey L. K., Edie C. F., Luco A. L., Mirchandani A., Karensbourg D. J., Jessop P. G. Switchable-polarity solvents prepared with a single liquid component. Journal of organic chemistry 2008, 73, 127-132

Phan L., Brown H., White J., Hodgson A., Jessop P. G. Soybean oil extraction and sepration using switchable or expanded solvents. Green chemistry 2009, 11, 53-59

Phan L., Chiu D, Heldebrant D. J., Huttenhower H., John E., Li X., Pollet P., Wang R., Eckert C. A., Liotta C. L., Jessop P. G. Switchable solvents consisting of amidine/alcohol or guanidine/alcohol mixtures. Industrial & engineering chemistry research 2008, 47, 539-545

Phan L., Jessop P. G. Switching the hydrophilicity of a solute. Green chemistry 2009, 11, 307-308

Podual K., Doyle III F. J., Pepppas N. A. Preparation and dynamic responsive of cationic copolymer hydrogels containing glucose oxidase. Polymer 2000, 86, 115-121

Ramanthan S., Block L. H. the use of chitosan gels as matrixes for electrically-modulated drug delivery. Journal of controlled release 2001, 70, 109-123

Rao Y., Amarne H., Zhao S., McCormick T. M., Martic S., Sun Y., Wang R., Wang S. Reversible intramolecular C-C bond formation/braking and color switching mediated by a

N,C-chelate in (2-ph-py)$BMes_2$ and (5-$BMes_2$-2-ph-py)$BMes_2$. Journal of the American chemistry society 2008, 130, 12898-12900

Roy D., Cambre J. N., Sumerlin B. S. Future perspectives and recent advances in stimuli-responsive materials. Progress in polymer science 2010, 35, 278-301

Roy I., Gupta M. N. Smart polymeric materials: emerging biochemical applications. Chemistry & Biology 2003, 10, 1161-1171

Ruhmann R. Polymers for optical storage-photorespoonsive polymers by structure variation in side-group polymethacrylates. Polymer international 1997, 43, 103-108

Sato O., Tao J., Zhang Y. Z. Control of magnetic properties through external stimuli. Angewandte chemie international edition 2007, 46, 2152-2187

Schild H. G. Poly(N-isopropylacrylamide): experiment, theory and application. Progress in polymer science 1992, 17, 163-249

Schmaljohann D. Thermo- and pH-responsive polymers in drug delivery. Advanced drug delivery reviews 2006, 58, 1655-1670

Senaratne W., Andruzzi L., Ober C. K. Self-assembled monolayers and polymer brushes in biotechnology: Current applications and future perspectives. Biomacromolecules 2005, 6, 2427-2448

Shibayama M., Norisuye T., Nomura S. Cross-link density dependence of spatial inhomogeneities and dynamic flucturations of poly(N-isopropylacrylamide) gels. Macromolecules 1996, 29, 8746-8750

Shiga T. Deformation and viscoelastic behavior of polymer gels in electric fields. Advances in polymer science 1997, 134, 131-163

Shriner R. L., Neumann F. W. The chemistry of the amidines. Chemical reviews 1944, 35, 351-425

Sortino S., Petralia S., Compagnini G., Conoci S., Condorelli G. Light-controlled nitric oxide generation from a novel self-assembled monolayer on a gold surface. Angewandte chemie international edition 2002, 41, 1914-1917

Starodoubtsev S. G., Saenko E. V., Khokhlov A. R., Volkov V. V., Dembo K. A., Klechkovskaya V. V., Shtykova E. V., Zanaveskina I. S. Poly(acrylamide) gels with embedded magnetite nanoparticles. Microelectronic Engineering 2003, 69, 324-329

Stuart M. A. C., Huck W. T. S., Genzer J., Muller M., Ober C., Stamm, M., Sukhorukov G. B., Szleifer I., Tsukruk V. V., Urban M., Winnik F., Zauscher S., Luzinov I., Minko S.

Emerging applications of stimuli-responsive polymer materials. Nature materials 2010, 9, 101-113

Such G. K., Evans R. A., Davis T. P. Control of photochromism through local enviroment effects using living radical polymerization (ATRP). Macromolecules 2004, 37, 9664-9666

Sutani K., Kaetsu I., Uchida K. The synthesis and the electric-responsiveness of hydrogels entrapping natural polyelectrolyte. Radiation physics and chemistry 2001, 61, 49-54

Suzuki A., Tanaka T. Phase transition in polymer gels induced by visible light. Nature 1990, 346, 345-347

Szabo D., Czako-Nagy I., Zrinyi M., Vertes A. Magnetic and mossbauer studies of magnetite-loaded polyvinyl alcohol hydrogels. Journal of colloid and interface science 2000, 221, 166-172

Szabo D., Szeghy G., Zrinyi M. Shape transition of magnetic field sensitive polymer gels Macromolecules 1998, 31, 6541-6548

Szabo D., Szeghy G., Zrinyi M. shape transition of magnetic field sensitive polymer gels. Macromolecules 1998, 31, 6541-6548

Tanaka T. Collapse of gels and the cretical endpoint. Physical review letters 1978, 40, 820-823

Tanaka T., Fillmore D., Sun S. T., Nishio I., Swislow G., Shah A. Phase transition in ionic gels. Physical review letters 1980, 45, 1636-1639

Tanaka T., Nishio I. Sun S. T., Collapse of gels in an electric-field. Ueno-Nishio S. Science 1982, 218, 467-469

Terech P., Weiss R. G. Low-molecular mass gelators of organic liquids and the properties of their gels. Chemical reviews 1997, 97, 3133-3159

Theato P. Synthesis of well-defined polymeric activated esters. Journal of polymer science part A: polymer chemistry 2008, 46, 6677-6687

Thornton P. D., McConnell g. Ulijin R. V. enzyme responsive polymer hydrogel beads. Chemical communications 2005, 59, 13-15

Tokarev I., Minko S. Stimuli-reponsive hydrogel thin films. Soft Matter 2009, 5, 511-524

Tomozei M., Balta Z. The restoration of a plate from a corselet (Iran, 17th centry). In Metal 98: Proceedings of the International conference on metals conservation.

Draguignan-Figanieres, France, 27-29 May 1998; Pennec S., Robbiola L., Eds.; James&James: London, 1998

Tsarevsky N. V., Matyjaszewski K. reversible redox cleavage/coupling of polystyrene with disulfide or thiol groups prepared by atom transfer radical polymerization. Macromolecules 2002, 35, 9009-9014

Ulijin R. V. Enzyme-responsive materials: a new calss of smart biomaterials. Journal of material chemistry 2006, 16, 2217-2225

Urry D. W. Physical chemistry of biological free energy transduction as demonstrated by elastic protein-based polymers. The journal of physical chemistry, B 1997, 101, 11007

Valentin N., Sanchez A., Herraez I. Analyses of deteriorated Spanish glass windows: cleaning methods using gel system. In ICOM Committee for Conservation, 11th Triennial meeting in Edinburgh, Scotland, 1-6 September 1996: Preprints; Bridgland J., Ed.; James&James: London, 1996

Van Durme K., Verbrugghe S., Du Prez F. E., Van Mele B. Influence of poly(ethylene oxide) grafts on kinetics of LCST behavior in aqueous poly(N-vinylcaprolactam) solutions and networks studied by modulated temperature DSC. Macromolecules 2004, 37, 1054-1061

Viswanathan N. K., Kim D. Y., Bian S., Williams J., Liu W., Li I., Samuelson L., Kumar J., Tripathy S. K. Surface relief structures on azo polymer films. Journal of materials chemistry 1999, 9, 1941-1955

Wang C., Tam K. C., Jenkins R. D., Bassett D. R. Potentiometric titration and dynamic light scattering of hydrophobically modified alkali soluble emulsion (HASE) polymer solutions. Physical chemistry chemical physics 2000, 2, 1967-1972

Wang G., Tian W. J., Huang J. P. Response of ferrogels subjected to an ac magnetic field. Journal of physical chemistry B 2006, 110, 10738-10745

Warda J., Brukle I., Bezur A., Kushel D. Analysis of agarose, carbopol, and laponite gel poultices in paper conservation. Journal of the American institute for conservation 2007, 46, 263-279

Wasserscheid P., Welton T. Ionic liquids in synthesis. VCH-Wiley: Weinheim, Germany, 2002

Watson P., Jones A. T., Stephens D. J. Intracellular trafficking pathways and drug delivery: fluorescence imaging of liveing and fixed cells. Advanced drug delivery reviews 2005, 57, 43-61

Weiss R. G., Terech P., Eds.; Molecular gels. Materials with self-assembled fibrillar networks; Springer: Dordrecht, the Netherlands, 2006

Wheller G. Alkoxysilanes and the consolidation of stone, Getty Publications: Los Angeles, 2005

Wolbers R. C. Cleaning painted surfaces. Aqueous methods; Archetype publications: London, 2000

Wolbers R. C. Notes for workshop on new methods in the cleaning of paintings, Getty Conservation Institute: Los Angeles, 1989

Wong V. N., Fernando G., Wagner A. R., Zhang J., Kinsel G. R., Zauscher S., Dyer D. J. Separation of peptides with polyionic nanosponges for MALDI-MS analysis. Langmuir 2009, 25, 1459-1465

Yager K. G., Barrett C. J. All-optical patterning of azo polymer films. Current opinion in solid state & materials science 2001, 5, 487-494

Yager K. G., Barrett C. J. Novel photo-switching using azobenzene functional materials. Journal of photochemistry and photobiology A 2006, 182, 4683-4690

Yamada N., Okano T., Sakai H., Karikusa F., Sawasaki Y., Sakurai Y. Thermo-responsive polymeric surfaces; control of attachment and detachment of cultured cells Makromolekulare chemie- Rapid communications 1990, 11 571-576

Yan Q., Zhou R., Fu C., Zhang H., Yin Y., Yuan J. CO_2-Responsive polymeric vesicles that breathe. Angewantde Chemie International Edition 2011, 50, 4923-4927

Yao L., Krause S. Electromechanical responses of strong acid polymer gels in dc electric fields. Macromolecules 2003, 36, 2055-2065

Zhang Q., Wang W., Lu Y., Li B., Zhu S. Reversibly coagulatable and redispersible polystyrene latex prepared by emulsion polymerization of styrene containing switchable amidine. Macromolecules 2011, 44, 6539-6545

Zhao B., Brittain W. J. Synthesis, characterization, and properties of tethered polystyrene-b-polyacrylate brushes on flat silicate substrates. Macromolecules 2000, 33, 8813-8820

Zhao Y., He J. Azobenzene-containing block copolymers: the interplay of light and morphology enables new functions. Soft matter 2009, 5, 2686-2693

Zhao Y., Luo Y., Li B., Zhu S. pH Responsivity and micelle formation of gradient copolymers of methacrylic acid and methyl methacrylate in aqueous solution. Langmuir 2011, 27, 11306-11315

Zhong Z., Song Y., Engbersen J. F. J., Lok M. C., Hennink W. E., Feijen J. A versatile family of degradable non-viral gene carriers based on hyperbranched poly(ester amine)s. Journal of controlled release 2005, 109, 317-329

Zhou K., Li J., Lu Y, Zhang G., Xie Z., Wu C. Re-examination of dynamics of polyeletrolytes in salt-free dilute solutions by designing and using a neutral-charged-neutral reversible polymer. Macromolecules 2009, 42, 7146-7154

Zrinyi M. Intelligent polymer gels controlled by magnetic fields. Colloid polymer science 2000, 278, 98-103

Zrinyi M., Barsi L., Szabo D., Kilian H. G. Direct observation of abrupt shape transition in ferrogels induced by nonuniform magnetic field. Journal of chemical physics 1997, 106, 5685-5692