LIVING POLYSTYRENE ANIONS TERMINATED WITH DIFULVENE

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By

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Abstract

This project proposal is focused on the development of a novel class of Viscosity Index improvers. A bench-top method for living anionic polymerization has been set up and tested in many aspects. A new difulvene derivative, 1,4-di(6'-6'-methyl-fulvyl)benzene, was synthesized. The living anionic polymer chain was terminated on this difulvene. Cyclopentadiene groups were formed in the middle of the macromolecule chain during the termination. A doubled molecular weight of polystyrene was obtained after the termination. The cyclopentadienes were then changed to other functional groups by Diels-Alder reaction with dimethyl acetylenedicarboxylate, ozonolysis of double bonds, and bromination and reaction with amine. The infrared spectra and nuclear magnetic resonance spectra of the resulting polymers showed new peaks for the new attached groups.

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Thesis Objective

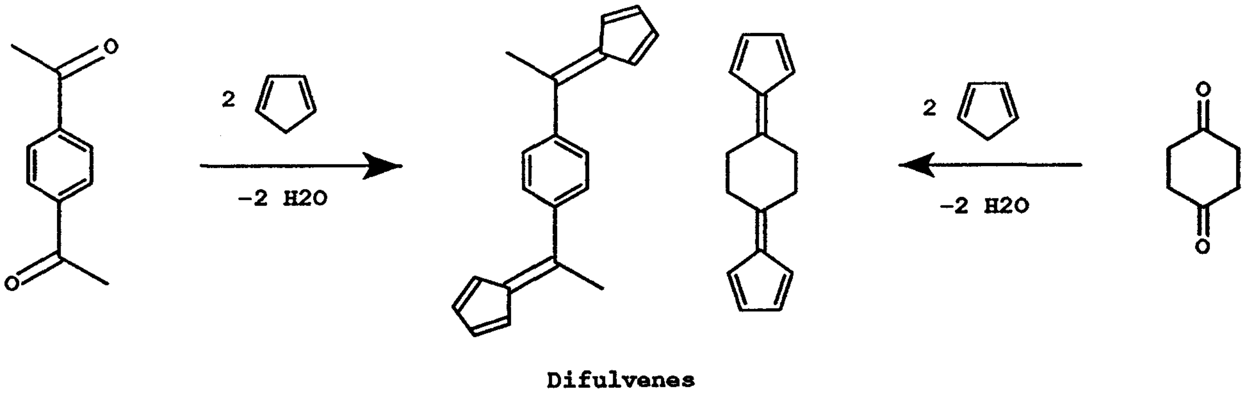
The synthesis and development of a novel class of polymeric lubricant additives is attempted. These additives are designed to produce high viscosities under high shear rates, a crucial property for modern gear and hydraulic oils. They may also serve as efficient pour point depressants and high temperature Viscosity Index improvers. The superior functions expected of the proposed additives is based on build-in reversible covalent aggregation.

The new additives are homopolymers and block copolymers of styrene, alkyl methacrylate, and isoprene, prepared by living anionic polymerization. They incorporate functional groups that should allow the polymers to link at the chain centers at low shear rate and low temperature, to give compact double-comb or star-shaped polymers with low intrinsic viscosity. Under higher shear rate, or at higher temperatures, these weak covalent links are designed to cleave reversibly. This is expected to increase the intrinsic viscosity.

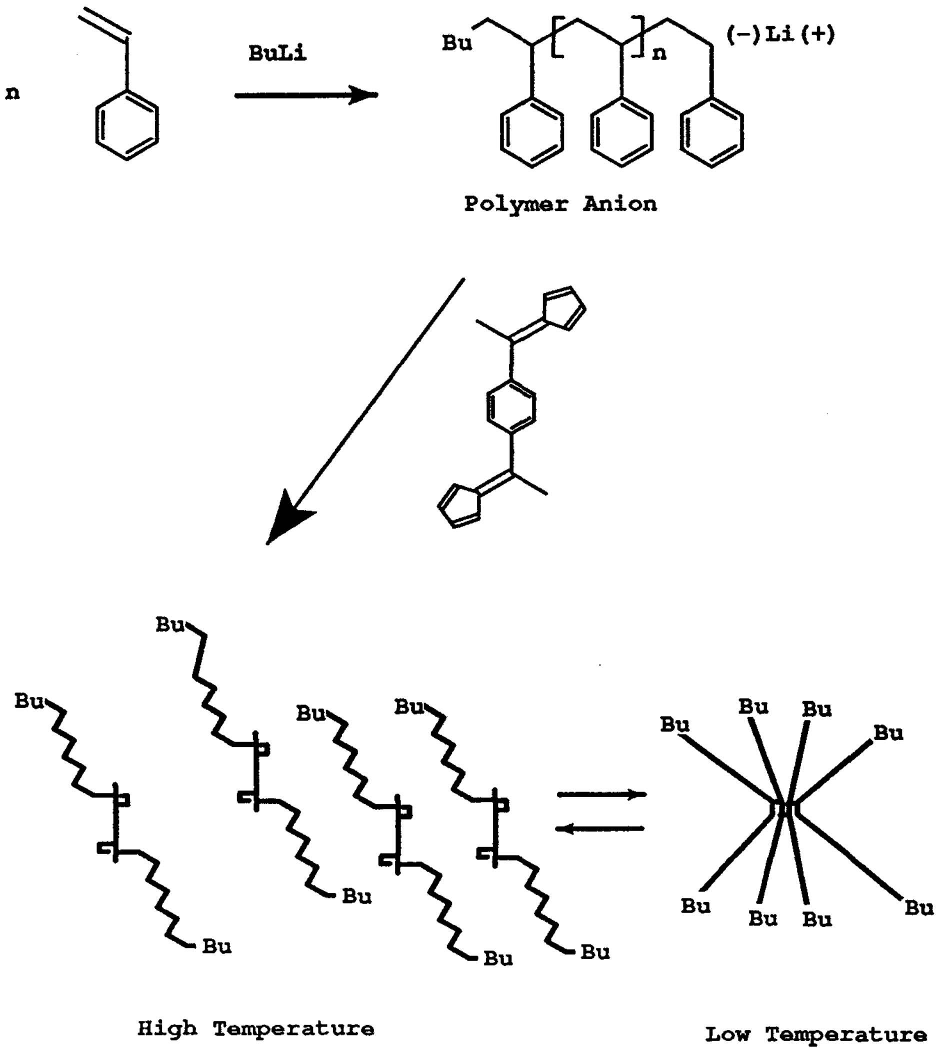
The proposed additives were prepared (see Scheme 2) by quenching two living polymer anions with a bifunctional difulvene (see Scheme 1) terminator, which thereby becomes incorporated into the center of the linear polymers. The quenching step simultaneously transforms the two fulvene functional groups into cyclopentadiene groups, which are ready to undergo reversible Diels-Alder coupling between the polymer molecules. This reversible reaction should establish the crucial shear and temperature dependent equilibrium between individual branches and double-comb polymer.

The preparation and characterization of this novel class of reactive polymers is described.

Scheme 1



Scheme 2



(Diels-Alder Equilibrium)

1. INTRODUCTION

1.1 Polymer Viscosity

Introduction

The chain character of polymers makes them different from their low molecular weight counterparts. The longer the chain, the higher the resistence to flow that a polymer solution or melt will experience. As a result the viscosity of a polymer solution is one of its most distinctive properties.

Two factors contribute to the viscosity of polymer melts and solutions : friction between chains sliding past each other, and temporary entanglements ("knots") of chains. In bulk polymers the empirical relation between the viscosity (η) of a polymer and its molecular weight (M) is

$$\eta = BM^{a}$$

with (a) = 1 without entanglement and (a) = 3.4 with entanglement, and there is a critical minimum chain length for entanglement. (B) is a preexponential factor. This relation is shown in Figure 1[1].

Polymer chains below this certain critical length move independently and produce a viscosity which depends on the first power of the molecular weight. In this case, for molecular motion in the absence of entanglement, a model theory, Debye viscosity equation, matched well with the above experimental equation,

$$\eta = \frac{\xi\, l_o^2\, \rho\, N_A\, n}{36\, M_o^2}$$

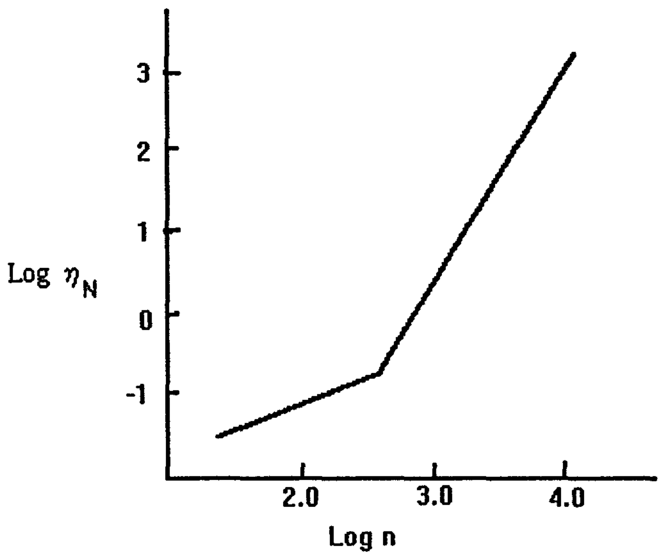


Figure1. The relation between viscosity and degree of polymer

Here, (ρ) is the density, (N_A)is Avogadro's number, n is the degree of the polymer, (M_0) is the molecular weight of the repeat unit, (l_0) is step length under Θ conditions, and (ξ) is segmental friction factor^2.

Θ condition is also called Flory condition. When a polymer dissolves in a solvent, polymer chains will form coils. A "good solvent" can swell the coil and increase coil dimensions. Conversely a "poor solvent" is a solvent which tends to decrease coil dimensions. Under Θ condition the poorness of the solvent exactly compensates for the excluded volume effect.

The presence of entanglements leads to an increase of the molecular weight dependence of viscosity. This is evident as a change of slope in Figure 1., not a discontinuity in the plot. With entanglements, (η) becomes considerably more sensitive to chain length. A simplified entanglement model, Bueche's model, assumed that when a polymer chain moves under shearing force with a velocity v_0, some fraction (s) of the velocity is transmitted to another chain entangled with the original. This is called primary coupling ($i = 1$). In the same fashion a fraction (s) of the velocity of the chain with first order coupling ($i = 1$) is transmitted to another chain. This is called second order coupling ($i = 2$). When a fraction (s) of the velocity is transmitted to the chain with the order of coupling of (i), Bueche[3] incorporated this into a quantitative theory, and predicts a 3.5-power dependence of viscosity on molecular weight, which is close to the observed 3.4-power dependence.

$$\eta = \frac{(\rho N_A)^2}{1728} \frac{lo^5 \xi}{Me^2} \left[\sum_i s^i (2i - 1)^{3/2} \right] n^{3.5}$$

whereas (i) is the order of coupling of Bueche's model, and (s) is the fraction through entanglement.

For polymer solutions, a similar empirical result is obtained, to relate the limiting viscosity number ($[\eta]$) of a solution, which has long been called the intrinsic viscosity of a polymer at a given temperature and solvent to molecular weight,

$$[\eta] = kM^a$$

It is known as Mark-Houwink equation. Here it is ($[\eta]$), rather then (η) itself which is proportional to M^a.

The intrinsic viscosity is defined as

$$[\eta] = \lim_{c \to 0} \frac{1}{c} \left(\frac{\eta}{\eta_0} - 1 \right)$$

where (c) is the concentration of a polymer solution, (η) is the solution viscosity and (η_0) is the pure solvent viscosity. (η) is the absolute viscosity of the polymer solution, (η/η_0) is the relative viscosity, and (η/η_0 - 1) is the specific viscosity. So $c^{-1}(\eta/\eta_0 - 1)$ is the reduced viscosity, called viscosity number and ($[\eta]$), the intrinsic viscosity is called limiting viscosity number. It has units of $\text{concentration}^{-1}$.

Since the intrinsic viscosity is a limiting value at infinite dilution, it is a parameter which directly reflects the molecular properties of the solute.

The constants (k) and (a) are called the Mark-Houwink coefficients for a system. The numerical values of (k) and (a) depend on both the nature of the polymer and the nature of the solvent, as well as the temperature. Here (M) is the viscosity average molecular weight M_v, which is defined as

$$M_V = \left[\frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i} \right]^{1/a}$$

and, Mv = Mw if a = 1.

There should be a straight line for the plot $\ln[\eta]$ versus lnM with slope (a) and intercept (lnk).

$$\ln [\eta] = \ln k + a * \ln M$$

Charles C. Han[4] derived a relationship of intrinsic viscosity and molecular weight from a blob theory[5] of a bead-and-spring model of a polymer molecule. According to the blob theory, the internal distances in a sufficiently short polymer even in a good solvent obey Gaussian statistics so that the intrinsic viscosity is of the same form as in a Θ solvent

$$[\eta]_o = k_o M^{1/2}$$

for molecular weights less than a given molecular weight, (M_1). For larger molecular weights, the intrinsic viscosity increases more rapidly with molecular weight. Using relationships for the radius of gyration and the hydrodynamic radius of a polymer and a dynamical argument of Weill and Cloizeaux, Han derives an equation for intrinsic viscosity that may be written as:

$$[\eta] / [\eta]_o = F (M / M_1)$$

where the function

$$F(M/M_1) = 1 \qquad \text{for } M < M_1$$

and

$$F(M/M_1) = 4/3\, x^{1/2} \{ x^{-2} (3 - 2/x) + 6 x^{1/5} [5/11 (1 - x^{-11/5}) - 5/16 (1 - x^{-16/5})] \} / [2 (1 - 1/3x) + 5/2 (x^{2/5} - 1) - 5/7 (x^{2/5} - x^{-1})]$$

for $M > M_1$, where $x = M / M_1$.

This relationship is shown in Figure 2.

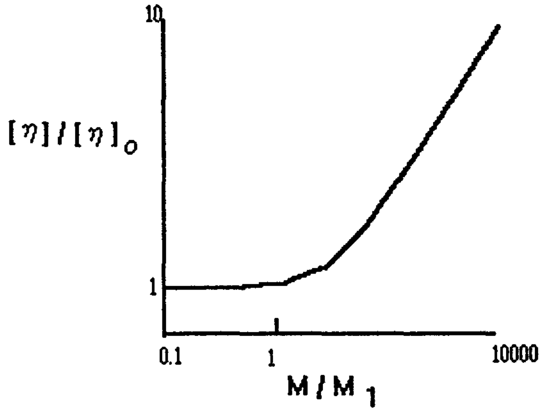


Figure 2. Han's relationship of intrinsic viscosity versus molecular weight

If we compare two polymers of identical molecular weight, one branched and the other linear, it is plausible that the branched one would show lower viscosity. Two considerations are included here. First, since the side chains contribute to the molecular weight, the backbone chain is shorter for the branched polymer. Second, the branched molecule is more compact and may actually be below the entanglement threshold in terms of chain length if not molecular weight. For these reasons, highly branched star-shaped polymers have a lower viscosity in solution compared with linear polymers of the same molecular weight. It can be assumed that if a star-shaped polymer can undergo cleavage to form linear chains, that under some conditions, the viscosity of the polymer solution will increase.

Viscosity Index improvers

Modern engine lubricants already contain a variety of polymeric additives designed to impart desirable properties to the mineral oil. The most significant applications of polymers as lubricant additives are as Viscosity Index(VI) improvers.

The commercial Viscosity Index improvers, or "thickeners", counteract the natural thinning of hydrocarbons at high temperatures or high shear rates, and thus reduce the dependence of lubricant viscosity on temperature and shear rate. Currently used VI improvers are linear, branched or star shaped hydrogenated polyisoprenes, and their block copolymers with styrene[6]. At low temperatures and shear rates, these polymers form aggregates of compact, poorly solvated coils with low intrinsic viscosity. With increasing temperature and shear rates, the coils expand, resulting in more entanglement and lower molecular weight and thus higher intrinsic viscosity.

Polyalkylmethacrylates are sometimes added to depress the pour point of hydrocarbon oils. They act by inhibiting , or slowing, the gelation of dissolved paraffin waxes at low temperatures[7].

The latest generation of viscosity modifiers are based on copolymers in which the VI improving effect by coil elongation, is augmented by a superimposed micellization. Selectively hydrogenated block-copolymers of styrene and butadiene or isoprene show phase separation of the polystyrene blocks. In lubricant stock at low temperatures colloidal polystyrene micelles are stabilized by the pendant hydrogenated polydiene blocks. These compact micelles disperse with increasing temperature to give an isotropic solution of the linear or star-shaped block copolymers. This thermal micelle-to-chain transformation leads to an even steeper intrinsic viscosity increase with temperature, compared with the homopolymers described above.

This reversible-micelle effect appears to be strongest for triblock copolymers comprising terminal hydrogenated polyisoprene blocks and a central polystyrene block. In the micellar state, the pendant aliphatic blocks are shorter compared to equal molecular weight diblock polymers, and thus cause less entanglement[8]. Micellization in such systems is driven by the positive cohesion between polystyrene blocks in hydrocarbon environments. This is a rather weak force, and accordingly the critical micelle temperature is centred around 60°C[9].

For example, an oil soluble hydrogenated polymer, polystyrene/butadiene-ethylene oxide block polymer, has been made as a new lubricant additive[10]. Anionic polymerization techniques were used to produce living poly(styrene-co-butadiene) chain, initiated with sec-BuLi, extended with ethylene oxide. The anionic end group was neutralized with glacial acetic acid to give the corresponding alcohol. The new block polymer has an oil soluble portion and a polar, oil insoluble portion. It proved to be a highly efficient, shear stable, viscosity index improver possessing significant dispersant/detergent properties.

This thesis aims at making a new class of star-shaped polymers containing weak covalent links. Thermal and shear induced cleavage should degrade these polymers into linear fragments of higher intrinsic viscosity.

1.2 Living Anionic Polymerization

There are several polymerization methods to synthesize macromolecules, such as anionic, cationic, radical, and condensation polymerizations. Living anionic polymerization is the method we use in this project.

The outstanding feature of homogeneous living anionic polymerization is the absence of any fortuitous chain termination step. This enables the following control in the synthesis of polymers:

(i) predictable molecular weight through control of initiator/monomer ratio;

(ii) narrow molecular weight distributions through proper adjustment of initiation versus propagation kinetics;

(iii) synthesis of true block copolymers by sequential addition of different monomers to the living polymer chains; and

(iv) formation of polymers with functional end groups by selective termination with appropriate reagents.

It is generally accepted that the anionic mechanism applies to those chain addition polymerizations in which the growing chain end has a negative charge (real or formal), and that these are initiated by bases of varying base strength.

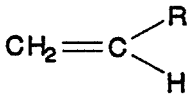
The classes of monomers involved in anionic polymerization are of three main types:

(i) monomers based on the carbon-carbon double bond (vinyl monomer);

(ii) heterocyclic monomers; and

(iii) monomers based on the carbon-heteroatom double (or triple) bond.

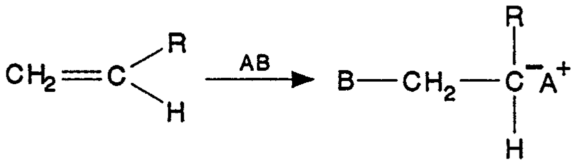
The kinds of vinyl monomers which undergo anionic polymerization are those with electron-withdrawing substituents such as the nitrile, carboxyl, and phenyl groups.



The electron-withdrawing R group helps stabilize the anion formed in the polymerization.

The initiator ions are of the following three types: alkali metals, aromatic complexes of alkali metals, and organoalkali compounds, mainly organolithium.

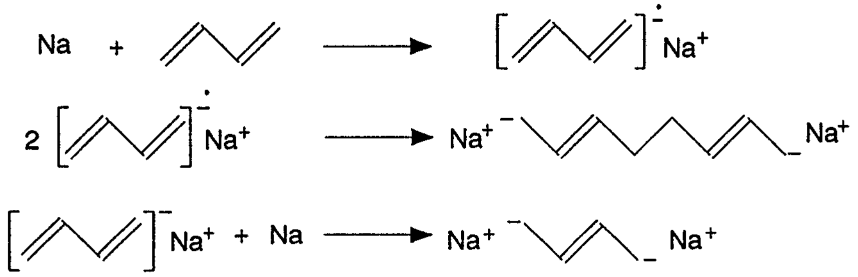
The general reaction is



here, AB is the basic initiator which breaks into a cation (A^+) and an anion (B^-) under the conditions of the reaction.

Initiating systems:

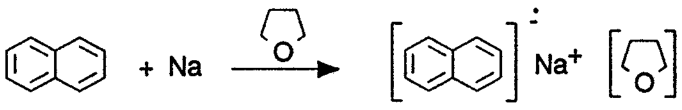
Sodium, an alkali metal initiator, initiates polymerization in the following manner:



First is an electron transfer from the sodium atom to the π orbital of the conjugated diene. It is followed by two alternative reactions of the initial radical-anions, radical coupling or a second electron transfer.

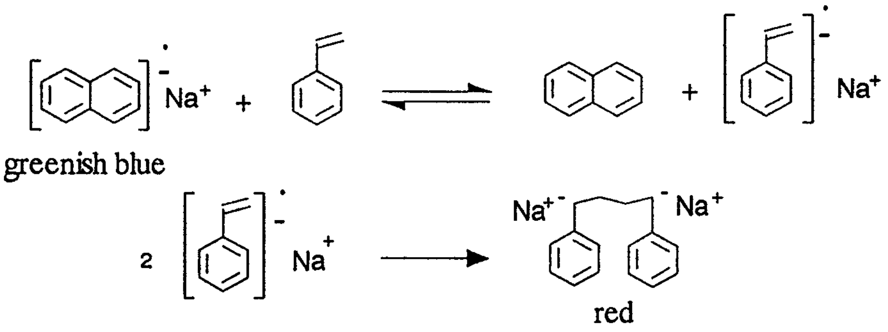
Of the aromatic complexes of alkali metals, **sodium naphthalenide** is the most common one. The first living polymer studied in detail was polystyrene polymerized with sodium naphthalenide in tetrahydrofuran at low temperatures[11]:

When alkali metals react with higher aromatics, in the presence of ether solvents, a colored solution is formed with no evolution of hydrogen:



Here the naphthalene radical-anion has an extra electron in the lowest unoccupied π–orbital and the solvent THF plays an especially important role in assisting the transfer of the electron from the sodium to the naphthalene and in stabilizing the complex through inter-orbital exchanges with the electrons available from the oxygen of the ether solvent.

The initiation step in this case is a rapid electron transfer step from the naphthalene to the styrene, as follows



Organoalkali compounds are different from the previous two groups in operating by a direct anionic nucleophilic attack rather than by an electron transfer mechanism. This leads to a mono-functional chain-growth reaction, which results in a better control of molecular weight distribution compared to the dianionic propagation involved in initiation by electron transfer.

Organolithium initiation is currently most widely used. One advantage is that organolithium species are soluble in both polar and nonpolar solvents, while higher organoalkali compounds generally require ethers as solvents.

Alkyllithiums in hydrocarbon solvents can often associate in groups of four or six, depending on their structure, and it is assumed that only the unassociated initiator molecules are active in initiation,

$$(\mathrm{RLi})_n \xrightleftharpoons{\mathrm{Ke}} n\,\mathrm{RLi}$$

$$\mathrm{RLi} + \mathrm{M} \longrightarrow \mathrm{RMLi} \xrightarrow{\mathrm{M}} \cdots$$

For the polymerization of styrene, the reactivities of the initiators are :

methyl > s-butyl > i-propyl > n-butyl and ethyl > t-butyl lithium,

while for dienes they are :

methyl > s-butyl > i-propyl > t-butyl > n-butyl and ethyl lithium.

The effect of solvents on polymerization rate is :

toluene > benzene > hexane > cyclohexane.

The initiators show the same relative reactivities toward styrene and the dienes, except in the case of t-butyllithium, which is a moderately fast initiator for the dienes but a very slow one for styrene. This low reactivity of t-butyllithium toward styrene can be ascribed to the steric hindrance between the two bulky substituent groups involved, i.e., t-butyl and phenyl.

Propagation reactions

The anionic propagation reaction, which is homogeneous in nature, is a simple bimolecular reaction between the growing chain and the monomer in principle. A general agreement is that the propagation rate is always first order in monomer, but rarely first order with respect to the concentration of growing chains. It would be expected that the propagation rate is affected by the nature of the medium (solvents), which could influence the character of the growing chain end, as well as the nature of the counterion introduced by the initiator, which may be associated with the living chain end.

1. Effect of solvent

In hydrocarbon solution metal ions, particular the lithium in n-BuLi, are essentially σ-bonded to the terminal carbon atom of a growing anionic polymer[12]. In solvating solvents such as ethers or amines, there is no significant tendency for aggregation of the propagating centers. The solvation of the metal cation leads to a more ionic character of the carbon-metal bond. However, complications can arise as a consequence of the simultaneous presence of ion pairs and free carbanions. Because of the exceptionally high reactivities of free carbanions and loose ion pairs compared to the modest reactivity of tight ion pairs, the course of the polymerization may be dominated by the presence of very small amounts of the two former species. In the anionic polymerization conducted in ether solvents[13,14], the free ion concentration is generally limited to 1% or less of the total active chain ends while the relative reactivities diminish in the sequence free anion > loose (solvent-separated) ion pair >> tight (contact) ion pair.

2. Effect of temperature

The temperature of polymerization seems to have little, if any, effect on the chain microstructure[15]. It was noticed, however, that the use of temperatures higher than 50°C led to some side reaction[16].

Chain transfer

The first study of an anionic chain transfer process was on the polymerization of 1,3-butadiene by sodium in toluene[17]. The reaction of toluene with the active chain end led to the formation of some benzyl sodium. This work was the first to demonstrate the important role of solvent in transfer reactions involving anionic active centers:

$$2\mathrm{Na} + n\mathrm{CH_2{=}CH{-}CH_2{=}CH_2} \longrightarrow \mathrm{Na^+\ {}^-[C_4H_6]_n^-\ {}^+Na}$$

$$\mathrm{Na^+\ {}^-[C_4H_6]_n^-\ {}^+Na} + 2\phi\mathrm{CH_3} \longrightarrow \mathrm{H[C_4H_6]_nH} + 2\phi\mathrm{CH_2Na}$$

The use of toluene resulted in a lower molecular weight than the value calculated from the monomer-initiator ratio.

Higginson and Wooding[18] also reported a transfer reaction to solvent for the case of the polymerization of styrene in ammonia initiated by potassium amide.

Gatzke[19] has investigated the chain transfer process involving toluene and poly(styryl)lithium at 60°C. A relationship between the number-average degree of polymerization and the transfer constant was derived:

$$x_n = [M]\,X/[PSLi] - C_{RH}\,[RH]\ln(1 - X)$$

where ([M]) denoted the monomer concentration, (X) the extent of conversion, [PSLi] the active center concentration, [RH] the concentration of toluene. The transfer constant C_{RH} was found to be $5 * 10^{-6}\ M^{-1}$.

When the transfer reaction of butadiene with the sodium counterion in a THF-toluene solution was studied[20], the presence of the ether was found to enhance the transfer reaction to the point where a transfer constant near unity was obtained.

Low molecular weight polybutadienes of various mixed microstructures are prepared[21] commercially via an anionic chain transfer process. These polymerizations use toluene as the solvent and transfer agent and lithium as the counter ion. The transfer reaction is promoted by the use of diamines, e.g., tetramethylethylene-diamine, or potassium t-butoxide.

Factors broadening the molecular weight distribution

There are two main factors which affect the molecular weight and its distribution: one is the effect of rates of initiation and propagation, while the other is the effect of chain termination or transfer.

1. Effect of slow initiation

In order to obtain a narrow molecular weight distribution, it is necessary to have a relatively rapid initiation rate compared to propagation rate.

The problem of slow initiation becomes critical when lithium alkyls are used to initiate anionic polymerization in hydrocarbon solvents because of their agglomeration. Polar additives dissociate the agglomerates and therefore speed up the initiation more than propagation. Such an effect is observed when a small amount of THF is added to styrene polymerized by butyllithium in benzene[22]. Meanwhile, polymerization initiated by a secondary alkyllithium compound gives more uniform molecular weight than those obtained on initiation with n-butyllithium[23]. This work implies that secondary derivatives are faster initiators than primary ones.

To avoid the difficulties arising from a slow initiation, it was proposed to add the monomer in two stages[24]. The first stage is designed to complete the initiation step while the molecular weight of the polymer is still low and, thus, to restrict variation in molecular sizes to an initially formed portion of the macromolecules. This method is more useful for the systems in which the depropagation of living polymers is sufficiently rapid, because then the depolymerized monomer again becomes available for further initiation. In the view of some investigators[25], in the absence of depropagation, no improvement in distribution is possible by restricting the reaction first to a fraction of the monomer and then adding the remaining portion later. Depropagation has a high activation energy; hence it is advisable to maintain a higher temperature at this stage of a small amount of monomer which has a low ceiling temperature, e.g., of α-methylstyrene, if its living oligomer acts as a rapid initiator.

2. Effect of impurities

In considering the effect of "chain termination" or chain transfer processes in anionic polymerization, a distinction must be made between the following possibilities: the partial destruction of initiator by impurities; the termination of growing chains by impurities, monomer, solvent, or bond rearrangements; and chain transfer reaction.

A successful preparation of nearly monodispersed polymers requires meticulous elimination of all impurities from the anionic system. The reagents, solvents, and walls of the reactor have to be rigorously purged, and it is imperative to remove any trace of moisture, oxygen, and of other electrophilic compounds. In detailed description of some techniques[26], the low molecular weight living oligomers are considered the best purging agents if the resulting dead material can be removed from the ultimate product. Alternatively, one may use other organometallic compounds, especially those which are reactive but not capable of initiating polymerization. For example, fluorenylsodium or lithium are most convenient purging agent for the final purification of styrene or α-methylstyrene, because these reactive salts do not initiate polymerization of either monomer.

It has been claimed[27] that anionically polymerized systems contain some relatively inert impurities which are not destroyed during the purging operation, and which eventually cause a slow killing of living polymers. Such a killing most probably arises from a slow reaction of living polymers with solvent. The purging operation cannot eliminate this difficulty; improvement of the procedure then requires a change of solvent or some judicial adjustments of the conditions maintained in the process, e.g., lowering the temperature of polymerization or increasing the monomer concentration.

It is obvious that impurities which terminate the growth of living polymers broaden the molecular weight distribution of the final product. Polymers which were terminated before they had attained their expected size contribute to the low molecular weight fraction, whereas those which retained their activity until completion of the conversion became longer than expected because the monomer not utilized by the others contributed to their own length.

Polymerization may be carried out in a reactor containing a solvent and an initiator (e.g., a low molecular weight living polymer) to which a monomer is added slowly with efficient stirring. Such a system is referred to as a continuous feed polymerization. Impurities present in the reactor and the solvent are destroyed by the initiator before the onset of polymerization. However, the loss of initiator does not affect the molecular weight distribution of the final high molecular weight product, although it increases the degree of polymerization. On the other hand, the distribution is affected by any damaging impurities present in the slowly added monomer because the living polymers are terminated continually in the course of their growth. So the most important thing is the purification of monomer in this case.

3. Effect of bifunctional initiators

The living polymers grow from both ends when using bifunctional initiators. The terminating agent attacks the growing ends indiscriminately and, hence, the reaction produces three types of polymers: dead polymers, polymers having only one growing end, and polymers possessing two growing ends. If killing is completed during the early stages of the reaction, polymerization results from the growth of two types of living polymers, the mono- and the bifunctional ones. The product then forms a mixture of two polymers, both virtually uniform in their molecular weight distribution, but one having twice the average molecular weight of the other[28].

In conclusion, the use of a monofunctional, in preference to a bifunctional initiator is beneficial when the impurity level is relatively high or when the spontaneous termination is not negligible. If a preparation is carried out in a meticulously purged system, a narrower distribution could be expected with a bifunctional initiator, especially if the sample finally prepared could be fractionated, and hence freed from the fraction derived from the partially killed initiator which has half the molecular weight of the bulk of the polymer.

4. Effect of inefficient mixing

The next essential requirement for a successful preparation of polymers of uniform size is the condition of constant spatial monomer concentration through the whole volume of the reactor. For a relatively slow propagation it should be possible to mix all the reagents at the onset of the reaction and eventually to maintain identical conditions in each volume element of the reactor during the course of polymerization. The temperature of the reacting mixture must be uniform; if not, local depletion of monomer, arising from the uneven rate of reaction, would lead to broadening of the distribution. Hence, stirring is necessary even if the reagents have been initially well mixed. Unfortunately, stirring and heat transfer become more difficult as the solution becomes more viscous.This makes the preparation of high molecular weight polymers even more difficult, especially if the rate of propagation is high.

When polymerization is rapid, it is necessary to supply the monomer gradually, i.e., its solution must be added continually or intermittently to the well-stirred reaction mixture. This again introduces some difficulties. For example, living polymers dissolved in the layers close to the points at which monomer is supplied are preferentially "fed", and hence grow longer than those located farther away.

1.3 Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) is one of several different types of high pressure (0-2000 psi) liquid chromatography. It can separate a mixture of polymers by passing a solution through an appropriate column. Tetrahydrofuran (THF) is the most common mobile phase for hydrophobic polymers whereas water containing an electrolyte (10^{-2} M) is used for water-soluble polymers. Columns are typically packed with spherical beads of crosslinked polystyrene. These beads have pores with diameters from 60 to 2000 Å. In GPC the separation occurs because molecules of different size penetrate the pores of the stationary phase to various degrees. The largest molecules are excluded from the pores to the greatest extent and, hence, are the first to emerge from the column. Progressively smaller molecules permeate the porous stationary phase to increasing extents and are eluted sequentially. The eluted material is monitored for solute by a suitable detector, and an instrumental trace of the detector output provides distinct peaks for well-resolved mixtures and broad peaks for a continuous distribution of molecular sizes.

There are several types of detector systems:

(a) Differential refractometer (DRI) is a concentration detector;

(b) UV or IR spectrophotometers, also are concentration detectors;

(c) DRI, UV, or IR in series with a viscometer detector to get $[\eta]$, and then using $[\eta]$ along with a universal calibration curve gives the molecular weight calibration curve.

When a concentration detector is used, a universal calibration curve, $\log[\eta]M$ versus retention volume (V_R), would be obtained. Here $[\eta]M$ is proportional to the hydrodynamic volume (V_H) of a polymer molecule in solution,

$$V_H = \Phi M [\eta]$$

for linear chains which are not too highly branched polymers. (Φ) is a universal constant for all polymer types. All polymer types should have the same universal calibration curve,

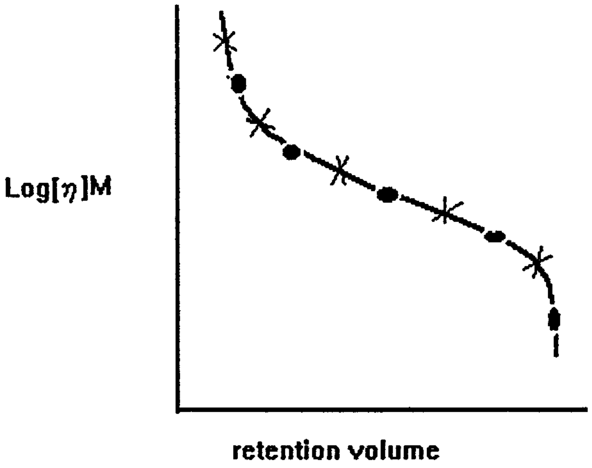


Figure 3. universal calibration curve

● polymer type 1 ; X polymer type 2

so for polymer 1 and polymer 2,

$$[\eta]_1 M_1 = [\eta]_2 M_2$$

Generally polystyrene synthesized by anionic living polymerization is used as narrow molecular weight distribution (MWD) standards. So for a polymer x for which narrow MWD standards are not available,

$$[\eta]_x M_x = [\eta]_o M_o$$

here, ($[\eta]_o$) and (M_o)are related to the polystyrene standards.

According to the Mark-Houwink equation for linear chains,

$$[\eta]_x = Kx\ Mx^{a_x}$$

so

$$[\eta]_x M_x = K_x M_x^{1+a_x} = [\eta]_o M_o = \phi_o$$

$$M_x = \left(\frac{\phi_o}{K_x}\right)^{1+a_x}$$

here, (K_x) and (a_x) can be found in the Polymer Handbook so one can use the universal calibration curve to find (M_x).

When using a mass concentration detector in series with a viscometer detector, ($[\eta]$) will be available, and use of the universal calibration curve then gives (M_x).

Commonly the retention volume (V_R) depends on LogM as shown in the molecular weight calibration curve (Figure 4).

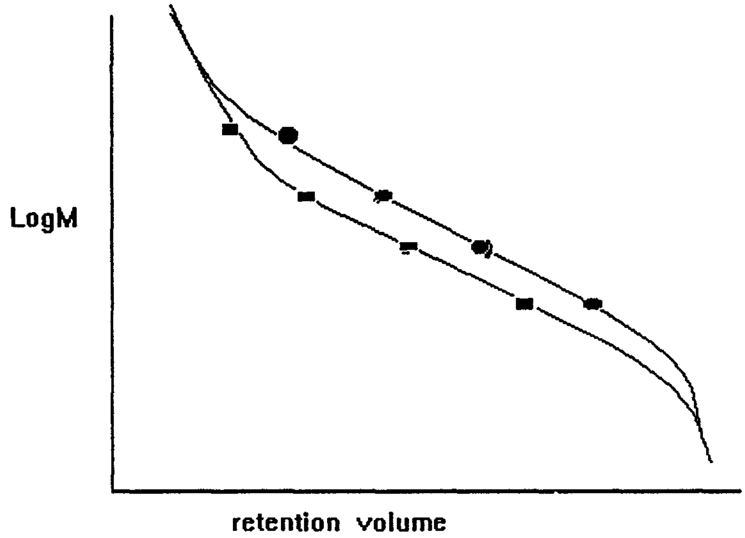


Figure 4. Molecular weight calibration curve

● polymer type 1 ; ▪ polymer type 2

so it is necessary to use different standards for different polymer types to use this curve directly. In the general case only narrow polystyrene standards are used.

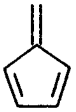
In GPC, the retention volumes of polymer molecules are determined by the effective hydrodynamic volume of the polymer molecule rather than the molecular weight. Polymer molecules with the same hydrodynamic volume will have the same retention volume no matter if they have same molecular weight. Linear polymer molecules have roughly similar entanglement behavior according to their molecular weights. The molecular weight of a linear polymer is therefore almost proportional to its hydrodynamic volume. Branched polymers, on the other hand, will have smaller hydrodynamic volumes than linear polymers of identical molecular weight. The scale of the difference in molecular weight depends on the number of branches. In this case GPC with linear narrow polystyrene standards can not be used to measure exact molecular weights.

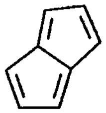
For branched polymers, **light scattering** techniques can be very useful as they measure the absolute molecular weight rather than the hydrodynamic volume.

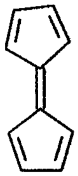
When a beam of light falls upon a particle of matter, the light with an intensity I_0 is scattered at an angle θ with a reduced intensity I_θ. In a solution, there is an excess scattering from the solute particles over the solvent alone. The scattering angle θ and the reduced light intensity I_θ vary with molecular weight.

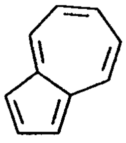
1.4 Fulvene Chemistry

Fulvenes, compounds possessing the structural feature (I), have been known since 1900. In definition[29], they are different from fulvalene (II), pentalene (III), azulene (IV), and related systems.

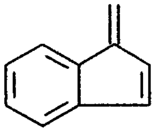

(I)

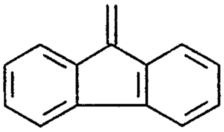

(II)

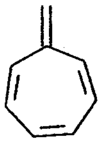

(III)


(IV)

(I) is referred to as a pentafulvene. Some more complicated fulvenes[30] are benzo-fulvene (V), dibenzo-fulvene (VI), heptafulvenes (VII), and triafulvenes like methylene cyclopropene-fulvene(VIII)[31].


(V)


(VI)

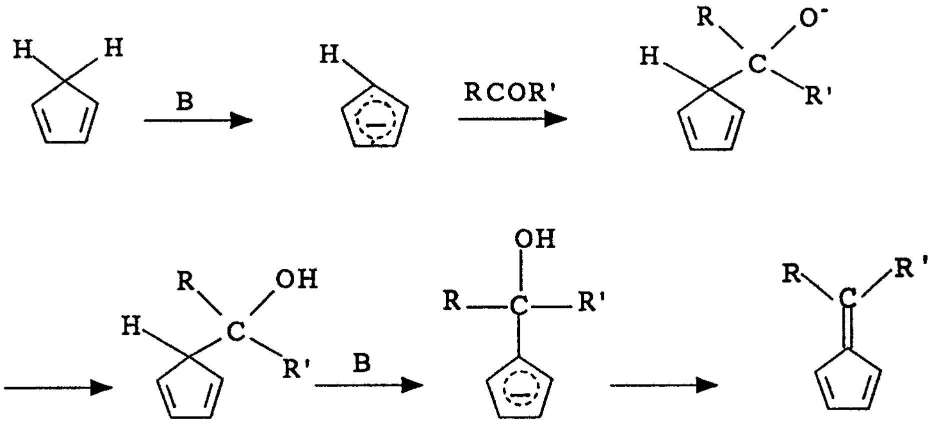

(VII)


(VIII)

1. Preparation of Fulvenes:

For the preparation of pentafulvenes, the common method is the base-catalyzed condensation of cyclopentadienes with aldehydes and ketones.

1) General reactions

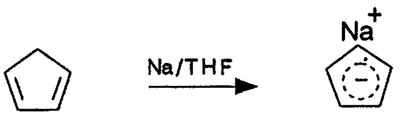


(IX)

The condensing agent (B)[32] serves both to form the cyclopentadienide ion, which effects nucleophilic attack at the carbonyl carbon atom, and also to catalyze the dehydration of the intermediate (IX), which is normally not isolated.

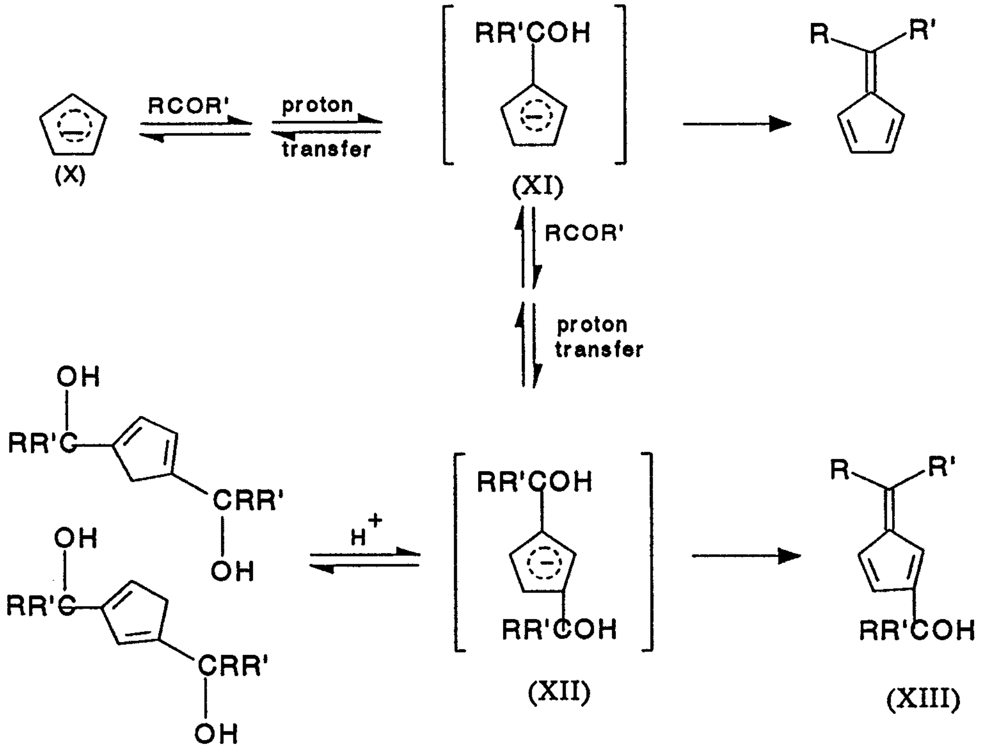
A variety of fulvenes with different R and R' substitutents have been prepared from cyclopentadiene and aldehydes and ketones in the presence of strong bases[33]. The bases usually are alkali metal hydroxides or alkoxides, such as KOH/MeOH, NaOEt/EtOH, or even sodium in THF.

In the reaction of ketones with cyclopentadienyl sodium(X)[34],



(X)

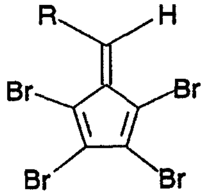
(X) reacts directly with ketones to form fulvenes



Here, the common intermediate ion (XI) can lose hydroxide ion irreversibly to give a fulvene or can condense with a second molecule of ketone to give the ion (XII) which loses hydroxide ion irreversibly to give the fulvenemethanol (XIII).

The relative yield of the two types of product are dependent on the concentration of the reactants and the base, the temperature, and the duration of reaction. Low reaction temperatures and concentrated reaction solutions favor formation of the fulvenemethanols. Sometimes fulvenemethanols are the main products.

Several 1,2,3,4-substituted fulvenes have been obtained by reaction of 1,2,3,4-substituted cyclopentadiene with aromatic aldehydes, for example 1,2,3,4-tetrabromo-6-phenylfulvene (XIV)[35] has been prepared from 1,2,3,4-tetrabromocyclopentadiene and benzaldehyde.



(XIV)

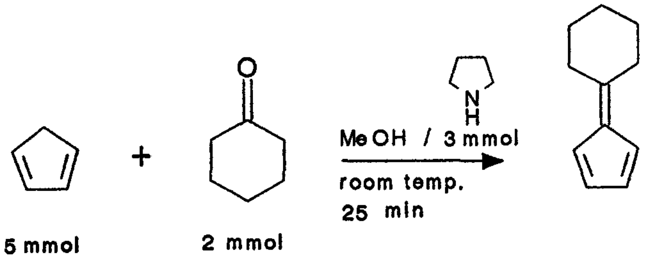
These reactions can occur in the absence of base. This fact must reflect the greatly enhanced acidity of the 1,2,3,4-tetrahalocyclopentadienes relative to the parent hydrocarbon.

2) Fulvene preparation in the presence of weak bases

The method was developed by Freiesleben[36], who prepared a variety of fulvenes in remarkably high yield by treatment of cyclopentadiene with aldehydes and ketones in the presence of primary or secondary amines, such as CH_3NH_2(aq), n-$C_4H_9NH_2$, and $C_6H_5NHNH_2$.

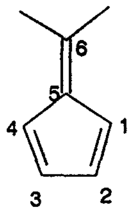
In 1983, a new weak base, pyrrolidine was chosen by Stone[37] to promote fulvene formation between cyclopentadiene and a host of carbonyl compounds. The effect of variation of temperature, solvent, and concentration upon the course of the reaction was examined qualitatively. Methanol proved to be the solvent of choice. Deuterium-hydrogen exchange experiments (between MeOD, starting materials, and product) were conducted and it was found that deuterium can be incorporated both before and after fulvene formation. The concentration is 1 ml of MeOH/1 mmol of substance. The temperature is room temperature.

For example, to prepare 6,6-pentamethylenefulvene, 1.5 mmol equiv of pyrrolidine was added to a solution of 1.0 mmol equiv of cyclohexanone and 2.5 mmol equiv of cyclopentadiene in methanol. The mixture was stirred under nitrogen at room temperature for 25 minutes. After adding in 1.6 equiv of acetic acid, the reaction mixture was diluted with ether and water to separate and purify the final products.



2. Structure and Properties

In structure there can be no question that there is very significant alternation in bond length in the five-member ring. That is $r_{12} = r_{34} \sim r_{56}$ and $r_{15} = r_{45} \sim r_{23}$,



The double bond between C_5 and C_6 will not participate in the Diels-Alder reaction. But this double bond makes C_6 active as an electrophilic position. When an anion attacks position 6, a stable six-electron aromatic ring will form.

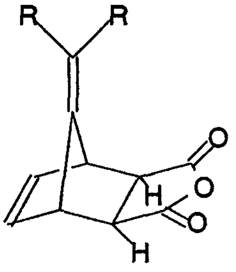
1) Diels-Alder reaction

The conditions for Diels-Alder reaction, generally the temperature and the time, vary a lot for different compounds.

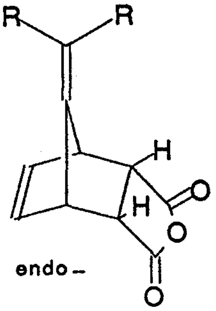
The dimerization of cyclopentadiene in neat state takes more than 24 hours to go to completion at room temperature. The Diels-Alder reaction between cyclopentadiene and dimethyl maleate in neat state can give a yield of 56% in 24 hours at room temperature[38]. Some of the dienophiles which bear substituents with stronger electronegativity can activate the reaction further. For example, N-isobutylmaleimide reacts with cyclopentadiene at 25°C in H_2O(emulsion) for 6 hours in quantitative yield[39]. When dibromomaleic anhydride and cyclopentadiene are refluxed in ether, a high yield of

Diels-Alder addition product is obtained in half an hour[40], while fumaryl chloride reacts with cyclopentadiene on standing at -10°C in dry ether for one hour to give 75% yield[41]. Some dienophiles with triple bonds can react more vigorously. When one mole of dimethyl acetylenedicarboxylate is mixed with one mole of cyclopentadiene at 0°C, the reaction is exothermic, and the product, dimethyl 3,6-methano-3,6-dihydrophthalate, can be obtained in high yield[42].

Fulvenes can participate both as diene and as dienophile in Diels-Alder reactions. The reaction of 6,6-dimethyl fulvene with maleic anhydride[43] appears to be complete during 16 hours at 25°C, and at least 94% complete during five minutes at 80°C, with a mixture of products, containing about equal amount of endo- and exo- adducts. Both adducts undergo retrogression, the endo- the more readily. These rearrange so that during a few hours in concentrated benzene solution at 80°C, an equilibrium mixture containing 85 to 88% of the exo- isomer is obtained.

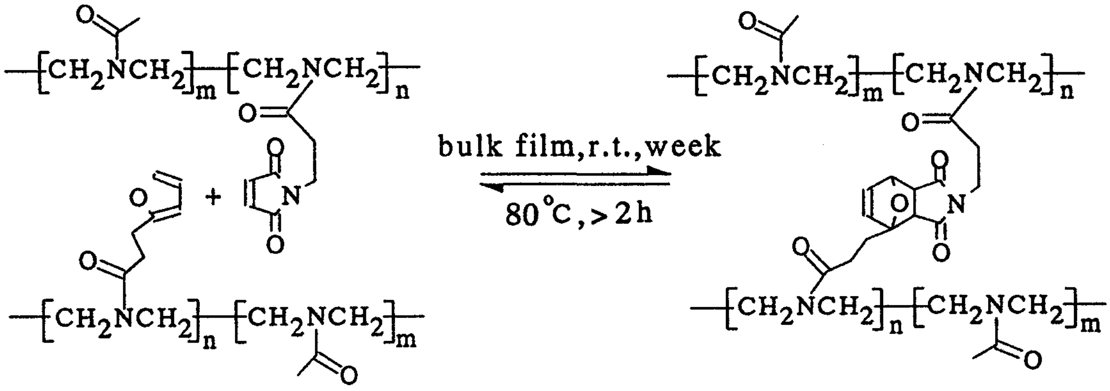


exo–



endo–

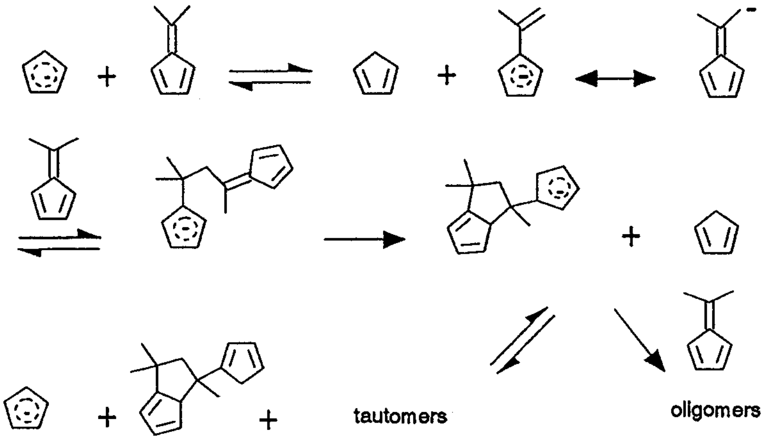
Diels-Alder reactions are reversible by thermal equilibrium. Dicyclopentadiene will dissociate into cyclopentadiene by heating to 160°C. This concept can be used to make new polymers with reversible covalent crosslinks. One good example is the study of reversible gelation of polyoxazoline[44]. In this example, polyoxazoline hydrogel was prepared by means of intermolecular Diels-Alder reaction between furan-modified poly(N-acetylethylanimine) (FPAEI) and maleimide-modified PAEI(MPAEI), which were synthesized from the partially hydrolyzed PAEIs by the reaction with furan- or maleimidecarboxylic acid, respectively, in the presence of dicyclohexylcarbodiimide. The gelation, cross-linking reaction, can be completed by placing a mixture of FPAEI and MPAEI in equal amount as a film in the dark for one week. The cleavage of the gel by retro-Diels-Alder reaction takes place in two hours at 80°C.



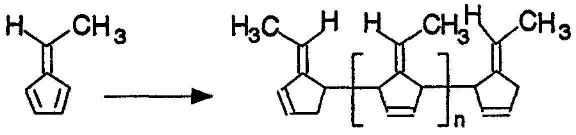
2) Polymerization

Simple fulvene itself is converted to a gelatinous polymer on standing at room temperature for a few hours[45]. In chloroform solution in the presence of hydrated stannic chloride or antimony trichloride[46], the polymerization of 6,6-dimethylfulvene was found to give a white polymer in 50%. Pyrolysis returned the monomer in 50% yield.

The above cationic polymerization can be prevented by traces of weak bases, such as tertiary amines. Strong nucleophilic reagents can cause anionic homopolymerization of fulvenes to form oligomers with n = 2 - 5[47].



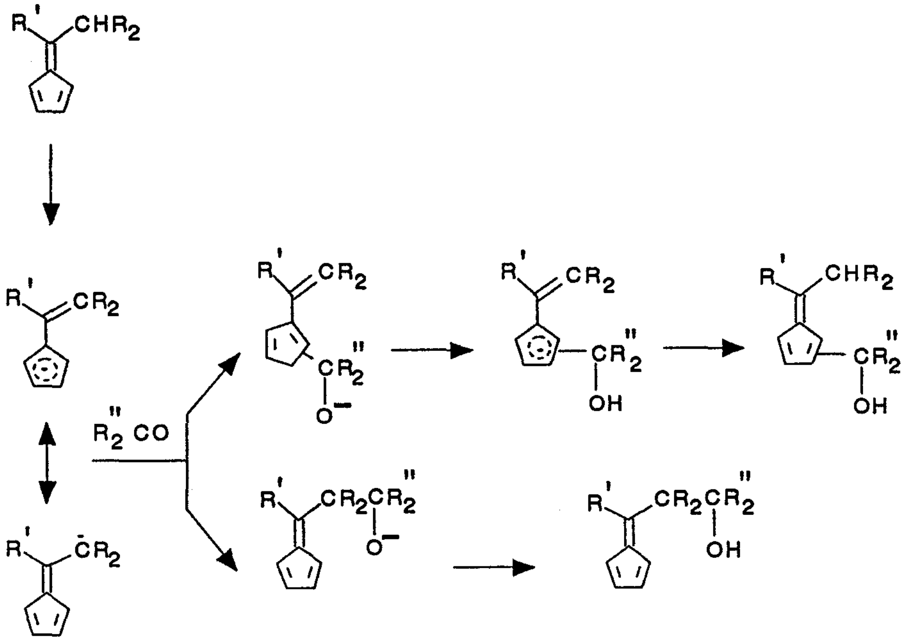
Sometimes polymerization of 6-methylfulvene can occur through 1,4 linkage at room temperature for several days[48],



Generally these reactions lead to oligomers or dimers, rather then polymers.

3) Condensation reactions

There are two possible routes for the condensation of fulvenes with carbonyl compounds in the presence of base. First, attack of base on C-6 could give rise to a cyclopentadienide ion, which could attack the carbonyl compound to form fulvenylmethanol. Second, in those cases where one of the C-6 substituents bears a hydrogen atom on the α-carbon atom, proton removal from this carbon could be followed by aldol condensation at the C-1, C-2, or C-6 positions,



Fulvenes accordingly are highly reactive compounds.

In this project 6,6'-dimethyl fulvene and 1,4-bis(2,4-cyclopentadiene-1-ylidene) cyclohexane were prepared according to the method in reference 37. A new difulvene, 1,4-di(6'-6'-methyl-fulvyl)-benzene was also synthesized. These fulvenes were used as terminators of living anionic polystyrene. This resulted in cyclopentadiene groups in the center of polystyrene. The new polymers were then characterized and several subsequent reactions were tested on them. These reactions are: Diels-Alder reaction, halogenation and ozonolysis.

2. EXPERIMENTAL

2.1. General introduction

2.1.1. Chemicals

Pyrrolidine, 99 %, b.p. 87-88°C, d 0.852, Aldrich Chemical Co.

Dicyclopentadiene, 95 %, b.p. 170°C, m.p. -1°C, Aldrich Chemical Co.

1,4-diacetylbenzene, 99 %, m.p. 111-113°C, Aldrich Chemical Co.

Styrene, 99 %, b.p. 145-146°C, m.p. -31°C, d 0.909, Aldrich Chemical Co.

α-methylstyrene, 99 %, b.p. 165-169°C, m.p. -24°C, d 0.909, Aldrich Chemical Co.

n-BuLi, 1.6 M solution in hexanes, Aldrich Chemical Co.

Trimethylchlorosaline, 98 %, b.p. 57°C, m.p. -40°C, d 0.856, Aldrich Chemical Co.

Acetic acid, 99.7 %, Fisher Chem.

Methanol, absolute, 99.9 %, b.p. 64-65°C, Baker Analyzed.

Dichloromethane, methylene chloride, 99.5 %, b.p. 39-40°C, Aldrich Chemical Co.

THF, tetrahydrofuran, 99.5 %, b.p. 65-67°C, BDH.

Sodium cyclopentadienylide, 2.0 M solution in tetrahydrofuran, Aldrich Chemical Co.

Methylamine, 40 wt. % solution in water, b.p. 48°C, Aldrich Chemical Co.

Petroleum ether, 35-60°C, Baker Analyzed

1,4-cyclohexanedione, 98 %, m.p. 77-78.5°C, Aldrich Chemical Co.

Diphenylacetic acid, 99 %, m.p. 147-149°C, Aldrich Chemical Co.

2,5-dimethoxybenzyl alcohol, 99 %, b.p. 122-125°C/1mm, Aldrich Chemical Co.

Dimethyl acetylenedicarboxylate, 99 %, Aldrich Chemical Co.

Dimethyl maleate, 96 %, b.p. 204-205°C, d 1.152, Aldrich Chemical Co.

Bromine, 99.5 %, BDH

Iodine, 99.8 %, BDH

Hydrogen peroxide, 29.0-32.0 % solution in water, BDH

Silica gel, 230-400 Mesh, EMSCIENCE.

Alumina, Basic, Brockman Activity 1, 80-200 Mesh, Fisher Chem.

2.1.2. Instruments

GPC, gel permeation chromatography, Waters 410 Differential Refractomer and Waters 441 Absorbance Detector, was the main equipment used in the measurement of the molecular weights of polymers.

NMR, AC200, is the main NMR equipment used for ^{1}H and ^{13}C NMR spectra.

FTIR, Furior Transfer infra-red spectrometer, Bio-Rad FTS-40, was used for IR spectra.

Mass spectrometer, VG 7070F equipped with a VG 2035 data system, was used to carry out all mass spectra. Electron impact (EI) were used in all cases.

2.2. Fulvene synthesis

2.2.1. Preparation and Stability of Cyclopentadiene

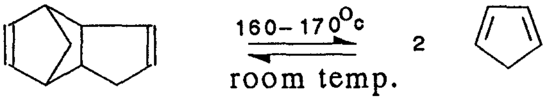
Cyclopentadiene dimerizes fairly rapidly at room temperature to form the dimer, dicyclopentadiene. Generally cyclopentadiene monomer is not commercially available. Several methods can be used to pyrolyse dicyclopentadiene to the monomer[49,50]. The pyrolysis apparatus that was chose is shown in Figure 5.

Commercial dicyclopentadiene (200 ml) was placed in a 500 ml two-necked round-bottom flask equipped with thermometer and an Friedrichs-type condenser. Through the condenser water at 50°C is circulated. The outlet of the Friedrichs condenser is connected to the side arm of a simple distilling head fitted with a nitrogen input adaptor and attached to a water-cooled condenser held in a vertical position. At the lower end of this condenser is a receiving flask immersed in a dry ice acetone bath.

The flask containing dicyclopentadiene is heated by means of an electric heating mantle to approximately 160-170°C. Cyclopentadiene (b.p. 40.0°C; m.p. -97.2°C) distilled smoothly at 38-46°C boiling temperature range and dicyclopentadiene refluxed in the Friedrichs condenser.

Fresh cyclopentadiene was used immediately or stored in the freezer below -25°C for upto one week.

The stability of cyclopentadiene and the speed of the dimerization have been tested by ^{1}H-NMR of cyclopentadiene samples which were stored at room temperature for different times.



Freshly obtained cyclopentadiene monomer has ^{1}H NMR($CDCl_3$, 200 MH_Z) δ 6.56(m, 2H), 6.47(m,2H), 2.98(dd, J=1.4H_Z, 2H) (see Figure 6a). Bulk cyclopentadiene has dimerized to about 5% at room temperature in 6 hours, and to about 20% (see Figure 6b) in 28 hours. The synthesis of fulvenes takes no longer than four hours. So cyclopentadiene is stable enough during the synthesis of fulvenes.

When the neat cyclopentadiene was heated to 45°C, 20 % of dimer was obtained in 3 hours.

2.2.2. Using amine as base to synthesize 6,6-dimethylfulvene (A)

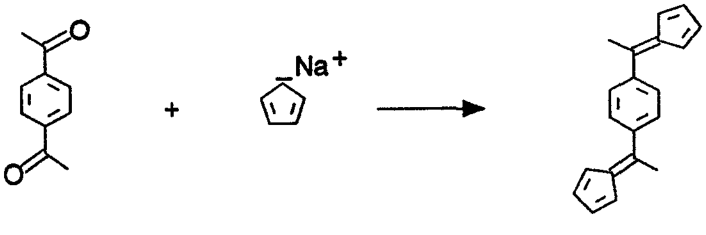
Methylamine $MeNH_2$ (1.5 ml, 0.015 mol, in 40% aqueous solution) was mixed with 8.2 ml (0.1 mol) of cyclopentadiene and 7.4 ml (0.1 mol) of acetone. After stirring for half an hour, a bright yellow two-phase solution appeared. The upper layerwas separated, dried with $MgSO_4$, and then distilled to separate and purify the products. Two fractions were obtained: one from 33-42°C distillation temperature (2.4 ml, light yellow); another from 42-42.5°C (2.3 ml, light yellow).

The purified 6,6-dimethylfulvene was a bright yellow liquid with a strong smell, b.p. 42-42.5°C, yield 20.4%. ^{1}H NMR($CDCl_3$, AC200 MH_Z) δ 6.50 (m, 4H), 2.20 (s, 6H), identical to the NMR of a commercial sample. The ^{1}H NMR showed that the first fraction was also 6,6'-dimethylfulvene with a trace of impurity.

2.2.3. Preparation of 1,4-di(6'-6'-methyl-fulvyl)-benzene (fulvene C) using cyclopentadienyl sodium

A solution of 0.35 g (2.2 mmol) of 1,4-diacetylbenzene in 35.0 ml of EtOH was slowly added to a flask containing 10.0 ml (2.0M, 20 mmol) of cyclopentadienyl sodium in 10.0 ml of EtOH over 1 hour under nitrogen at room temperature. The reaction was then continued for another half hour.

The reaction mixture was then concentrated by evaporating the solvent. 50 ml of chloroform was then added and the solution extracted three times with 25 ml of distilled water. After evaporating the chlorofrom, an oily red brown product was formed.



(C)

The crude product weighed 0.30 g, while the theoretical yield is 0.567 g. But the ^{1}H NMR of the product has very weak signals from (C) and a lot of by-product peaks. The first reason is the absence of separation and purification of the final product. The second reason is that the basicity of the catalyst, cyclopentadienyl anion is so strong that some polymerization occured.

2.2.4. Synthesis of difulvenes by using pyrrolidine

1) Synthesis of 1,4-di(6'-6'-methyl-fulvyl)-benzene (C) using pyrrolidine

According to Stone's method[37], pyrrolidine is a very effective reagent to promote fulvene formation between cyclopentadiene and carbonyl compounds.

To a solution of 3.2g (20 mmol) of 1,4-diacetylbenzene and 3.5 ml (42.7 mmol) of cyclopentadiene in 20 ml of reagent grade methanol, 8.3 ml (100 mmol) of pyrrolidine was added. The mixture was stirred under nitrogen at room temperature. Analysis by silica-gel TLC at different time showed four hours at room temperature to be the best reaction time. At that time there are more fulvenes and less precipitate which is not easy to dissolve into ether during the following separation. After 4 hours 6.2 ml (110 mmol) of acetic acid was added to the solution. The reaction mixture was diluted with ether and water (30 ml each). The aqueous portion was washed with ether (3 x 30 ml) and the combined organic phase was washed with water and brine(15 ml each), then dried over

$MgSO_4$, and concentrated by rotary evaporation. Finally silica-gel column chromatography (silica gel, 200-430 mesh, 200g, 60 cm x 31 mm) was used to separate and purify the final products. From 100% petroleum ether elution, the difulvene(III) (needle crystal, 503.2 mg) was obtained with orange-yellow color, whereas in the following 5% diethyl ether in petroleum ether elution, the monofulvene(D) (needle crystal, 1.53 g) was obtained with orange-red color. There was some viscous material with deep red color left at the top of the column which was supposed to be oligomers of fulvene and fulvenes with an hydroxy substituent. The difulvene was then recrystallized two times from heptane.

The final product (C) $C_{20}H_{18}$, MW 258, is orange-yellow needle crystals with melting point 167-168^{o}C under nitrogen. The yield is 10 %. TLC (100% petrolium ether, silica gel) R_f 0.43. The elemental analysis calculation for formula $C_{20}H_{18}$ is C 92.98% and H 7.02%, found: C 92.70% and H 7.32%. ^1H NMR ($CDCl_3$, 200 MH_Z) 7.40 (s, 4H, H_e), 6.58 (m, 6H, H_d, H_d', H_c), 6.22 (m,2H, H_b), 2.59 (s, 6H, H_a) (see Figure 7a). For ^{13}C NMR ($CDCl_3$, 200 MH_Z) and its assignment, please see Figure 8a. In Figure 9a the 2-D ^1H-^{13}C shift correlation NMR spectrum shows more detail information about the NMR assignment. Mass spectrum, m/z (relative intensity) 258 (M^+, 100), 243 (81), 228 (40), 215 (17), 202 (17), 189 (9), 165 (18), 152 (13), 115 (8) (see Figure 10a). In FTIR spectrum there is no carbonyl group (see Figure 11a).

1-(6'-methyl-fulvyl)-4-acetylbenzene (D)

This compound (D) $C_{15}H_{14}O$, MW 210, is a main by-product during the synthesis of the above difulvene with a yield of 30%. It is an orange-red needle crystal with melting point 92-93^{o}C. TLC (100% petroleum ether, KODAK Chromagram Sheet, silica gel) R_f 0.045. The elemental analysis result is C 85.32% and H 7.00% while the formula calculation is C 85.68% and H 6.71% with formula $C_{15}H_{14}O$. ^1H NMR ($CDCl_3$, 200 MH_Z) δ 7.98 (d, 2H, $H_{e'}$, H_e), 7.47 (d, 2H, $H_{f'}$, H_f), 6.62 (m, 2H, H_d), 6.50 (m,1H, H_c), 6.11 (m, 1H, H_b), 2.64 (s, 3H, H_a), 2.55 (s, 3H, $H_{a'}$) (see Figure 7b). For ^{13}C NMR and its assignment, please see Figure 8b. In Figure 9b the 2-D ^1H-^{13}C shift correlation NMR spectrum shows more detail information about the NMR assignment. Mass spectrum, m/z (relative intensity) 210(M^+, 43), 195 (13), 167 (100), 152 (40) (see Figure 10b.). In FTIR spectrum a sharp peak of carbonyl group appeared (see Figure 11b).

2) Further conversion of monofulvene to difulvene

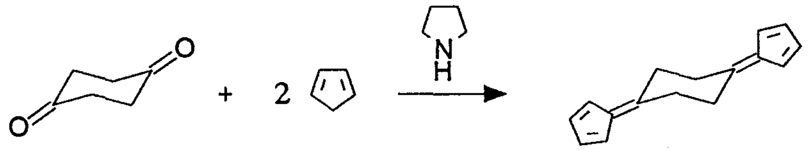
In the two step synthesis of difulvene the first step forming monofulvene is relatively easier and faster than the second step forming the final difulvene. It was attempted to prepare difulvene from monofulvene to increase the yield of difulvene here.

In a 50 ml flask, 957.4 mg (4.56 mmol) of the above monofulvene (D) , 0.95 ml (11.4 mmol) of cyclopentadiene, and 5.0 ml of MeOH were mixed, and then 0.60 ml (6.84 mmol) of pyrrolidine was added. The reaction took about four hours under nitrogen. The concentration ratio of difulvene to monofulvene was almost the same as the above preparation reaction, about 1 to 3. After column separation 78.8 mg of difulvene (C) and 200.0 mg of monofulvene (D) were obtained. Therefore the yields did not change.

3) Synthesis of 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane (K)

Using the same method, a difulvene, 1,4-bis(2,4-cyclopentadiene-1-ylidene)-cyclohexane (K) was reported to be prepared by M.L.McLaughlin[51] et.al. As a functional terminator of living polystyrene, it was produced here according to McLaughlin's procedure.

The title compound was prepared in one step by condensation of 2.3g (20 mmol) of 1,4-cyclohexanedione with 4.1 ml (50 mmol) of freshly distilled cyclopentadiene catalyzed with 4.2 ml (50 mmol) of pyrrolidine in 10 ml MeOH at room temperature. The reaction time is 20 minutes. The final bright yellow product was purified and collected by vacuum sublimation at 100°C, 0.1 mmHg. The yield is 547 mg, 12 %.



(K)

Compound (K) $C_{16}H_{16}$, MW 208, is a bright yellow solid with m.p. 167-168°C under nitrogen. The elemental analysis is C 92.35 % and H 7.79 %, while the formula calculation is C 92.26 % and H 7.74 %. ^{1}H NMR ($CDCl_3$, 200 MH_Z) δ 6.55 (m, 8H), 2.89 (s, 8H) (see Figure 7c.). For ^{13}C NMR and its assignment please see Figure 8c. Mass spectrum, m/z (relative intensity) 208 (M^+, 100), 193 (22), 178 (23), 165 (25), 153 (13), 141 (13), 128 (18), 115 (21), 91 (13), 77 (13) (see Figure 10c). In FTIR spectrum there is no carbonyl group (see Figure 11c).

To compare with compound (C), compound (K) has a boat shape while (C) has a rigid planar structure. When they are used in termination of living anionic polystyrene, two polymers with different functional center will be formed. It will be interesting to test the difference in physical properties, for example, viscosity.

2.3 Living anionic polymerization

Living anionic polymerizations require absenve of moisture, oxygen, carbon dioxide, and electrophilic impurities. To reach these conditions, reaction vessels need to be very clean and all reagents need to be purified very well.

2.3.1. Flask cleaning

Three methods have been tried to clean the polymerization flask. In the first method, the flask was dried in an oven at 170°C for five hours. Then **5% Me_3SiCl in THF** was poured into the flask to about one third of the flask. Then the contents were refluxed for about twelve hours. After the refluxing the flask was rinsed three times with pure THF.

As a second cleaning method, flaming the flask was tried. The flask was dried in the oven for 24 hours, then was flamed for about half an hour under nitrogen before the polymerization.

The third method is to use a solution of 0.5 ml of purified styrene and 1.0 ml of n-BuLi in 20 ml of hexane to rinse the whole reaction apparatus before experiments. Sometimes more n-BuLi is needed to keep the orange living polystyrene color during the rinse.

The third method was found to be the best method.

2.3.2. Purification of solvent and monomer

THF is constantly refluxed over potassium metal under purified nitrogen. A small amount of benzophenone was added because the resulting organometallic compound reacts more efficiently with impurities, such as moisture, than the alkali metal itself. Moreover, the appearance of the characteristic blue color serves as an indicator demonstrating the absence of impurities. The THF was then distilled into another flask. Into this flask, sufficient living polystyrene oligomer was added to maintain a yellow color. This living polystyrene can kill the residual impurities in the THF. The THF was then distilled directly into the reaction flask and used immediately.

The commercial styrene monomer was purified through an alumina column first to remove inhibitors, and was then dried over CaH_2 for 24 hours under nitrogen. Then the styrene was distilled under vacuum (50 mbar) at 80°C into a flask with triethylaluminum (Et_3Al). The organometallic compound, triethylaluminum, further reacts with any trace polar impurities. A second vacuum distillation from triethylaluminum to a clean, dried flask gave pure styrene.

The terminators, trimethylchlorosilane (after one distillation), or difulvenes (after over night vacuum drying), were dissolved in dry THF, degassed under vacuum, and covered with purified nitrogen or argon. They were introduced into the living polymer solution by syringe injection.

2.3.3 Using excess organometallic compound to destroy the impurities

Before the anionic polymerization, one drop of purified styrene was injected into 100 ml of THF followed by 100 μl of n-BuLi. A yellow color formed. When all of the 100 μl of n-BuLi reacted with impurities, the yellow color disappeared. Then another one drop of styrene and 100 μl of n-BuLi were added until the yellow color stayed for more than one hour. Generally, it takes 200 μl of n-BuLi to purify the THF prior to the anionic polymerization.

2.3.4. Titration of n-BuLi

Commercial butyllithium reagent is usually accompanied by a lot analysis, but often even freshly obtained solutions have obviously deteriorated, being colored and cloudy, and most butyllithium solutions deteriorate after the container is opened. For use in anionic polymerization, an excess or a deficiency of butyllithium is often detrimental. Thus precise analysis of the real concentration of an alkyllithium reagent is desirable.

Two convenient titration methods have been used to determine the concentration of n-BuLi.

Diphenylacetic acid[52]. A sample of 0.5007g (2.36 mmol) of diphenylacetic acid was weighed into a flask fitted with a magnetic stirrer and sealed with a septum and dissolved in 15 ml of purified THF. The flask was flushed with nitrogen. n-BuLi was added dropwise from a syringe until a stable yellow colored end point was reached. At the end point, 1.60 ml of n-BuLi had been added.

Diphenylacetic acid has the advantage of being a solid, stable on storage and easily weighed. The yellow color indicates formation of lithium α-lithiodiphenylacetate after all the carboxyl proton is consumed. The experiment showed the concentration of n-BuLi is 1.47 M, whereas the commercial label is 1.6 M.

$$(C_6H_5)_2CHCOOH \longrightarrow (C_6H_5)_2CHCOO^-Li^+$$

colorless

$$\downarrow$$

$$(C_6H_5)_2C^-Li^+COO^-Li^+$$

yellow

Another titration, **2,5-dimethoxybenzyl alcohol**[53], was used to check out the precision of the above result: 2,5-dimethoxybenzyl alcohol (143 μl, 1 mmol) was injected into a sealed flask containing 6 ml of purified THF. N-BuLi was added dropwise with a syringe until the solution had just changed to a pink color. 0.70 ml of n-BuLi was used at the end point, and the concentration of n-BuLi was calculated to be 1.43 M.

The origin of the red color is uncertain, but it appears to be due to the presence of dianions in the solution.

The relative difference of the two titrated concentrations is

$$2(1.47-1.43)/(1.47+1.43) = 2.7\ \%$$

2.3.5. Procedure of living anionic polymerization of styrene

The living polystyrene can also be terminated with some other terminators containing protons, such as H_2O, MeOH, and trimethylchlorosilane (Me_3ClSi), and the orange color will disappear immediately and a viscous, clear dead polymer solution formed. A white polystyrene powder can be obtained by precipitating the THF polymer solution into an excess of methanol. Two reprecipitations are needed to remove solvents and inorganic by-products, such as LiCl.

Polystyrene samples were dried under vacuum for several hours before NMR or IR testing.

2.4. Polystyrene terminated with fulvenes

2.4.1. with 6,6'-dimethylfulvene (polystyrene 1)

N-BuLi (200.0 μl, 1.43 M) was injected into a flask with 100 ml of THF at room temperature. Ten drops of styrene were added. An orange color appeared immediately. The solution was then immersed into a dry-ice/acetone bath. At -78°C 1.50 ml of styrene was added dropwise. There was no change in the orange color. After five minutes 100 μl of polymer sample was removed through a syringe to measure the molecular weight. Then 25.0 μl of 6,6'-dimethylfulvene (2.175×10^{-4}mole) was added. A brown red color appeared immediately. The color changed to light yellow after two hours. The solution was then warmed up to room temperature and acetic acid was added to neutralize the solution. The yellow color became lighter.

In GPC the molecular weight of polystyrene before the termination and after the termination were similar. The results* are:

	Mn	Mw/Mn
Predicted molecular weight	4800	
Before fulvene termination	6200	1.16
After fulvene termination	5640	1.14

* the sample No. is sl139

Before the termination the living chain concentration is

$$1.50\text{ml} \times 0.909 \text{ g/ml} / 6200 = 2.20 \times 10^{-4} \text{ mole}$$

So when 2.175×10^{-4} mole of 6,6'-dimethylfulvene was added there should be 100 % termination with fulvene.

When this solution was heated at 45°C for two days, there was no change in molecular weight during this time, indicating that no Diels-Alder coupling of two chains had taken place.

2.4.2. with 1,4-di(6'-6'-methyl-fulvyl)-benzene (polystyrene 2)

The reaction procedure was the same as above.

When 0.5 mole equivalent of fulvene (C) was injected into the orange living polystyrene solution, a dark red color appeared immediately. In the GPC test a double molecular weight peak appeared and it reached the highest value in one hour while there was still a small amount (around 10 to 15 %) of polymer with the original molecular weight peak (see Figure 12).

2.5. Further reactions

2.5.1. Thermo-reversible Diels-Alder coupling of polystyrene (2) (polystyrene 3)

Title polystyrene (300.0 mg, sample No. sl169A, Mn 53,350) was dissolved in 3.0 ml of THF in a test tube. This solution was then heated at 45°C for 24 hours. The same test was also repeated by using toluene as solvent and the mixture was heated at 90 °C for 24 hours. The change of molecular weight distribution during the reaction was followed by the GPC test. In GPC no molecular weight increase was observed, but a thermo-cleavage and decrease of molecular weight was apparent (see Figure 13).

2.5.2. Diels-Alder reaction between dimethyl acetylenedicarboxylate (DMAD) and polystyrene terminated with difulvene (polystyrene 4)

The experiment was designed to make a star-polymer. 1.581 g of the title polystyrene (sample No. sl167B, Mn 12,940, 1.22 x 10^{-4} mole) was dissolved into 6 ml of dimethoxyethylene. Dimethyl acetylenedicarboxylate (16.0 µl, 1.30 x 10^{-4} mole) was added. The solution was heated at 80°C for several days. A change of molecular weight distribution was not observed by GPC.

Two samples of 500.0 mg of the title polystyrene (sample No. sl165A, Mn 18,270, 2.74 x 10^{-5} mole) were dissolved in THF and toluene separately. Dimethyl acetylene dicarboxylate (200 µl, 16.2 x 10^{-3} mole) was added to each. The THF solution was heated at 45°C for 3 days, the original light yellow color of polymer remained, and there was no change in molecular weight distribution in GPC. The toluene solution was heated at 90°C for 3 hours and the light yellow color disappeared. After the reaction the new polystyrene (polymer 4) was precipitated two times by methanol to purify it.

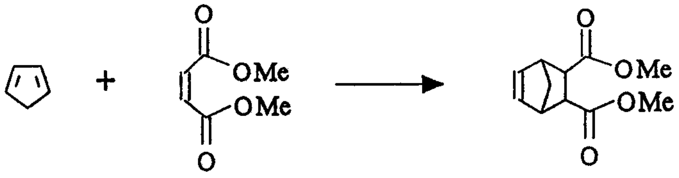
In ^{1}H NMR of polymer 4 there is a multiple peak at 3.8 ppm which demonstrates the existence of the methoxy group from DMAD (see Figure 14). The existence of carbonyl group from DMAD in polymer 4 was proved by FTIR (see Figure 15, middle curve).

In Figure 15 the IR spectra are after subtraction from polystyrene standard since polystyrene has a strong sharp peak at 1600 λ^{-1} wavenumber which may overlap the small carbonyl absorbance. After the subtraction the peaks appearing there would be the absorbance from carbonyl groups in polystyrene samples.

2.5.3. Diels-Alder reaction between cyclopentadiene and dimethyl maleate (product 5)

Cyclopentadiene (1.0 ml, 12 mmole) was added to 1.50 ml (12 mmole) of dimethyl maleate at room temperature, and the reaction was followed by ^{1}H NMR tests at different reaction times. The reaction was also repeated at 45°C.

This reaction proceeded slowly at room temperature. At room temperature, the major Diels-Alder product with about 2% dicyclopentadiene by-product was formed in 3.5 hours (see Figure 16a). When the reaction temperature was increased to 45°C, the Diels-Alder reaction was complete in one hour.



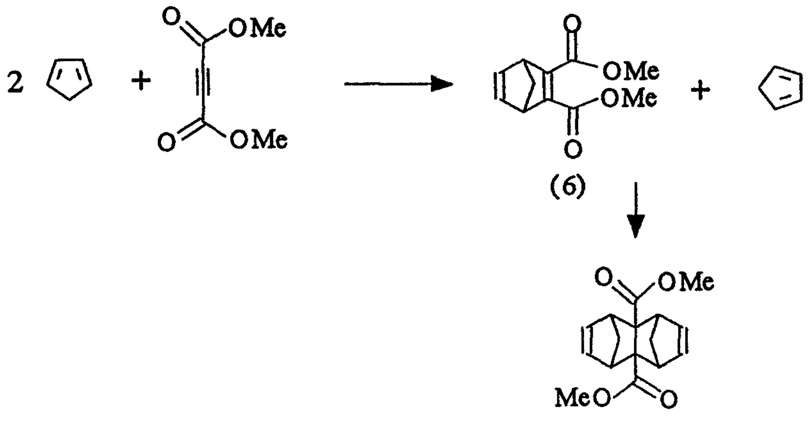
5

2.5.4. Diels-Alder reaction between cyclopentadiene and dimethyl acetylene dicarboxylate (product 6)

Dimethyl acetylene dicarboxylate (0.75 ml, 6 mmol) was added dropwise to 1.0 ml (12 mmol) of cyclopentadiene slowly at 0°C. A vigorous exothermic reaction occured immediately. When the reaction mixture became stable, the solution was warmed up to room temperature or 45°C. The reaction rate at different temperatures was monitored by

^{1}H NMR. At room temperature ^{1}H NMR showed a mixture of Diels-Alder reaction product (6) and cyclopentadiene in one hour.

The second Diels-Alder reaction (product 7) was very difficult even after increasing the reaction temperature to 45°C for several hours (see Figure 16b).



(6)

(7)

The one to one reaction to get product (A) was examined by the second reaction: 1.5 ml (12 mmol) of dimethyl acetylenedicarboxylate was added to 1.0 ml (12 mmol) of cyclopentadiene at room temperature and pure product (6) was obtained in one hour for ^{1}H NMR spectrum (see Figure 16c).

2.5.5. Using Lewis acid, aluminum chloride, as catalyst in Diels-Alder reaction (polystyrene 8, 9)

Lewis acid, aluminum chloride, has been reported in Diels-Alder reaction as a catalyst.

Polystyrene (2) (293.5 mg, sample No. sl169C, Mn 35,330, 8.31 x 10^{-6} mole) was dissolved in 6 ml of dimethoxy ethylene. The solution had a light yellow color due to some fulvene group in the polymer. To this solution 20.0 mg of **monopotassium acetylenedicarboxylic acid** (1.31 x 10^{-3} mole) and 20.0 mg of **aluminum chloride** (1.50 x 10^{-3} mole) were added. The light yellow color disappeared and the clear solution changed to white cloudy. The mixture was heated at 70°C overnight and remained cloudy. In the GPC there was no change in molecular weight distribution. The final polymer (polystyrene 8) had a broad and deep peak around 1600 λ^{-1} in IR. It may be the absorbance of carbonyl group in acid. But the strong signal seems to show that some acetylenedicarboxylic monomer is present.

Polystyrene (2) and (8) (200.0 mg) were dissolved in 3.0 ml of benzene separately. A capillary viscometer was used to measure the viscosity. There was no difference in time for the solution going through the two lines of the viscometer for the two sample.

Polystyrene (2) (303.2 mg, sample No. sl169C) was dissolved in 6 ml of dimethoxy ethylene. **Dimethyl acetylene dicarboxylate** (200 µl) and 20 mg of $AlCl_3$ were added. The solution was heated at 70°C for overnight. The light yellow color didn't disappear as it did in the absence of aluminum chloride, but it changed to a deep yellow in one hour. All $AlCl_3$ powder dissolved and the solution was clear. After two times precipitation from methanol a new polystyrene (9) was obtained. It had no change in MWD of polymer in the GPC. In ^1H NMR it has a multiple peak at 3.8 ppm which is the same result as in Figure 13. It also had a carbonyl absorbance in IR which is shown in Figure 15, the bottom curve with sample No. sl185d.

2.5.6. Ozonolysis of the cyclopentadiene group of polystyrene (2) (polystyrene 10,11)

This can be easily performed by using ozone generator. At -78°C, when ozone was bubbled through the THF solution of polystyrene (2) which has a yellow color, the color changed to clear in just a few seconds. The clear THF solution was stable when keeping the ozone flow for about one hour. A long term ozone flow will have time to cleave the polystyrene backbone. The formed ozonide was then treated with hydrogen peroxide, H_2O_2, in 30 % aqueous solution. Then added in several drops of concentrated hydrogen chloride until the pH of the solution was around 3-4. A new polystyrene (10) was obtained after two-fold precipitation from methanol. The carboxylic group of polystyrene (10) was observed in FTIR (see Figure 17 the bottom curve). In GPC an increase of molecular weight wasn't observed (see Figure 18, curve a and b).

When using a capillary viscometer to check the change of viscosity of benzene solution of polymer (2) and (10), there was no difference in viscosity.

When using methylene chloride as solvent for ozonolysis, the yellow color of the solution disappeared first in a few seconds and a green color followed up and the solution became cloudy and viscous like a gel at -78°C. Polystyrene (11) was obtained following the above procedure. In the FTIR a carbonyl group absorbance was observed (see Figure 17 the middle curve). In the GPC a broadening of molecular weight distribution of polystyrene (11) shown, and the longer time ozone was used, the wider the MWD (see Figure 18, curve c and d).

2.5.7. Test of bromination and iodination of cyclopentadiene and styrene(12)

1.0 ml of styrene monomer (8.7 mmol) was mixed with 65 mg of iodine (0.25 mmol). THF(1 ml) was added in to dilute and dissolve I_2. The solution was heated at 70°C in room light for one hour and the brown color of iodine changed to light pink. The pink color disappeared totally in 3 hours. The solution sample was not viscous.

When 0.50 ml of hexane solution of bromine (18.83 mmol) was dropped into 1.60 ml of styrene (13.98 mmol), the deep red color of bromine disappeared immediately and the reaction was exothermic.

0.50 ml of cyclopentadiene (6 mmol) was mixed with 65 mg of iodine (0.25 mmol) in 1 ml of THF. The mixture was then heated at 45°C under room light for one hour and the dark brown color of iodine changed to green brown. The solution became strongly viscous and dark green after overnight.

When 0.10 ml of bromine was dropped into 0.50 ml of cyclopentadiene with 2 ml of THF, the brown color of the solution didn't change. When this solution was heated at 45°C under room light for overnight, the color changed to dark red and the solution was viscous (product 12).

2.5.8. Bromination and iodination of the cyclopentadiene group in polystyrene 2 (polystyrene 13a, 13b, 14a, 14b)

Polystyrene 2 (500.0 mg, sample No. sl169E, Mn 40,370, 1.24 x 10^{-5} mole) and 0.60 ml of bromine in methylene chloride (5.65 x 10^{-5} mole Br_2) were added into 3 ml of methylene chloride. The solution was stirred at room temperature under room light for two hours. The solution color changed from deep brown to light yellow. The new polystyrene (13a)was then precipitated two times from methanol to wash out Br_2 left.

When the same amount of iodine was used instead of bromine, the deep brown color of the solution caused by I_2 did not lighten in several days. A new polystyrene (13b) was obtained after two times precipitation.

After the bromination and iodination the two new purified polystyrenes (13a, 13b) were dissolved in toluene separately. An excess amount of methylamine ($MeNH_2$) in 40 wt. % aqueous solution was added. When the two-phase mixture was stirred at 40°C for several minutes, the solution containing iodo-polystyrene became cloudy while this happened in the bromo-polystyrene after several hours. These reactions were run overnight. The samples were checked by GPC to test a possible increase in molecular weight. Then several drops of concentrated sodium hydroxide were dropped in until pH was around 10. Two new polystyrene (14a from 13a, 14b from 13b) were obtained by two time precipitation from methanol. The changing of the functional group from halogen to methylamine was suggested by ^1H NMR. In the ^1H NMR of polymer 14a and 14b there was a small singlet peak at 2.4 ppm which might be the amine methyl groups (see Figure 19).

3 RESULTS AND DISCUSSIONS

3.1 Methods for Living Anionic Polymerization

1. Reaction vessels

1) High vacuum system

Any experimental work involving living polymers and kinetic studies of their formation and growth, requires meticulous cleaning of the apparatus used in such investigations. The growing ends and the initiators of anionic polymerization are extremely reactive and are readily deactivated by moisture, oxygen, carbon dioxide, proton-donor impurities, etc. It is often necessary to carry out the experiments on a high-vacuum line, to eliminate, as far as possible, greased stopcocks and replace them by breakseals and constrictions, and to destroy by some suitable means all damaging contaminants adsorbed on the walls of the apparatus. Figure 20 shows a typical one[54] which can permit rigorous experimental conditions.

It is primarily composed of an oil pump (1) capable of producing a vacuum of the order of magnitude of 10^{-1} to 10^{-2} mmHg. This pump acts as a fore pump for the mercury diffusion pump (2) which reduces the pressure in the system to 10^{-6} mmHg. The liquid nitrogen trap (3) is used to condense any condensable gases so that the pressure measured by the McLeod gage (4) is that of the noncondensable gases, such as oxygen and nitrogen. With such an apparatus, it is possible to remove all impurities that can react with either the initiator or the growing anionic polymers produced.

According to these ideas, a high-vacuum line as shown in Figure 21 was set up. (1) is a general vacuum oil pump which can produce a vacuum to 10^{-3} mmHg. (2) is the silicone oil diffusion pump which can produce a maximum vacuum to 10^{-6} mmHg. A cold liquid nitrogen trap is used to protect the diffusion pump (2) from getting polluted by condensable gases in the system, while trap (4) is used to protect the pump (1). (5) is a McLeod gauge for vacuum measurement.

The crucial reason for using the living anionic polymerization method is to get 100 % living chains and predictable molecular weight. Using a high vacuum apparatus can not only satisfy the above two demands but also produce very narrow polydispersities.

When this high vacuum line was used the major problem was the complexity of its operation. The reaction conditions were so strict that one experiment generally took two to three days.

2) Bench-top reactor

To simplify the experimental procedure, a bench-top reactor has been tried and developed to meet the above two crucial factors for this research.

It consists of a flask, with a septum, sitting on a stirrer. Purified nitrogen (through two NaOH drying towers and two $CaSO_4$ drying towers) or argon was used during the anionic polymerization. Every reactant was added by syringe through the septum.

The reactor was rigously cleaned and dried prior to each polymerization, as explained in the experimental section.

2. Stirring bar and mixing

A critical requirement of living anionic polymerization is efficient stirring to achieve constant spatial distribution of monomer during polymerization.

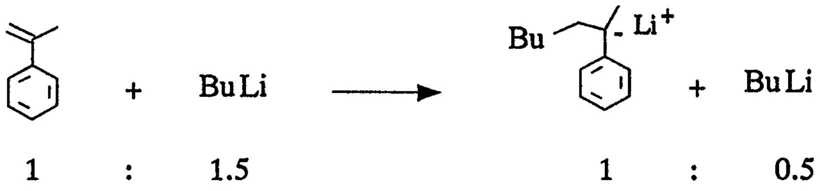
A teflon stirring bar was tried first. The white Teflon stirring bar was attacked slowly by n-BuLi during the anionic polymerization reaction to become grey black. This protective, grey black layer, preventes further damaging reaction. However, the coating sometimes can be damaged bit by friction with the glass flask during the stirring, and the fresh Teflon surface exposed can again react with organometallic initiators, like n-BuLi. Since this happened only occasionally, the "black" teflon bar is still a good choice.

In other experiments, the Teflon stirring bar was seals into glass. The glass coating makes the stirring bar easy to clean and perfectly inert to attach by BuLi. A glass belt can be added on the middle of the new coated glass stirring bar in attempts to make it rotate smoothly.

Commercial glass coated bars have also been tried. They have a symmetric shape and rotate stably. The inside metallic magnetic bar, however, is too heavy to rotate fast and also shows high friction due to the contact of the glass of the bar with glass of the flask bottom. Another problem with the commercial glass bar is that it is easily broken during the stirring because the glass covering can not be annealed during the manufacturing.

3. Using excess organometallic compound to destroy the impurities

Some organometallic compounds which do not initiate the polymerization of the investigated monomer can be used for the final purification of reaction system. In the solution of α-methylstyrene with n-BuLi the equivalent ratio of reactants was one α-methylstyrene to one and one half n-BuLi,



and after the fast reaction, the ratio of products was two β-butyl-α-methylstyrene anions to one n-BuLi.

The addition product of α-methylstyrene with n-BuLi is effective to purify the THF solvent. However, extensive chain transfer was observed in this experiment:

To the above purified THF solvent, an amount of n-BuLi as initiator was added, followed by 1 ml of styrene. A orange-yellow color (the color of living polystyrene) appeared soon. 100 μl of this living polymer solution was removed and terminated. Another three times 1 ml of styrene were added, with 100 μl of solution being removed after each 1 ml of styrene. The total yield of polymer was 95 %.

The molecular weight of these four sequential polystyrene samples should increase by the same amount each step, if the reaction is a normal living anionic polymerization. This was not found.

	Mw/Mn	Mn(experi.)	Mn(calc.)
Sample No.1 (1ml styrene)	1.38	8500	
Sample No.2 (2ml styrene)	1.39	10600	17050
Sample No.3 (3ml styrene)	1.40	12300	25580
Sample No.4 (4ml styrene)	1.39	12740	34100

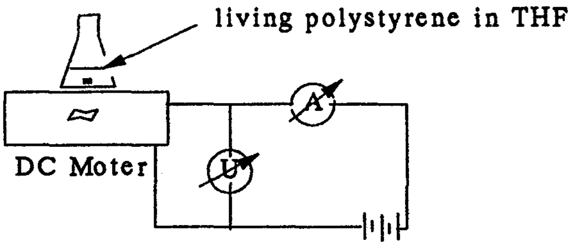
The molecular weights of the polymer products were much lower than expected. A possible reason is the chain transfer from the living polystyrene chain to α-methylstyrene (formed by reacting with impurities) occured.

To avoid chain transfer reaction, another organometallic compound, styrene itself with n-BuLi, was used in the same way. This was described in the experimental section. Generally, it takes 200 μl of n-BuLi with two drops of styrene to purify 100 ml of THF before the anionic polymerization. In this case only 25 % of n-BuLi reacted with the drop of styrene to give the yellow color. Another 75% of n-BuLi was used to react with impurities. The n-BuLi can react faster than β-n-butylstyrene anion with impurities. In this case chain transfer is not a problem since β-n-butylstyrene anion itself is the initiator. So this is a good and effective method.

4. Determination of concentrations of growing chains

When using difulvene as terminator of anionic styrene polymerization, it is important to add in a quantitative amount of difulvene to make sure that one mole of difulvene can react with two mole of living chain molecule. So it is necessary to test the concentration of living polystyrene molecules before addition of the difulvene.

The first method that was tried was to set up a new electrical equipment, a viscometer, to measure the viscosity of living polymer in THF solution in situ.



There is a stir bar in the flask containing living polystyrene in THF solvent. The stirrer driver is a DC Motor. The current and voltage of the motor is monitored by meters. The more viscous the solution becomes, the more power needed. To keep the stir bar at constant RPM (rotation per minute), the provided power (I x U) has to be adjusted. With a proper calibration the changing viscosity can be read directly and instantaneously from the current and volt meters.

Before the anionic polymerization the pure THF solvent is non-viscous. When the polymerization occurs the solution becomes viscous gradually. The solution viscosity depends on the concentration and molecular weight of polymers in the solution. In a pure system the polymer concentration can be controlled by the amount of initiator added in. Since our flask anionic polymerization system is not very exact and the amount of impurities that consume the initiator is unknown, the real amount of initiator that is used in the initiation of polymerization is unknown, as is the concentration of living polystyrene. The viscometer described above can be used in this case to measure the viscosity and so the concentration of living chain. So long as the concentration of living chain is known, terminators, such as difulvenes, can be added stoichiometrically to control the final polymer products. A group of data for this viscometer is listed below:

sample	RPM(min^{-1})	U(V)	I(mA)	P(I x U)(mW)
water	437	1.70	75	127.5
THF	439	1.66	68	112.9
3.0 g p.s.* in 100.0 ml THF	442	1.93	98	189.1
10 g p.s.* in 100.0 ml THF	440	1.39	42	58.4

* the two polystyrene samples are the same, MW 20,000.

When the viscosity of the THF solution increased, the power needed increased first but then decreased and it was even lower than the pure THF solvent. In this experiment the power needed is to drive the stir-bar. Since the stir-bar used here was a glass-coated magnetic bar, two opposing factors influence the power. One is the viscosity of the solution, the more viscous the more power needed; another is the frictional force between the glass bar and the glass flask bottom, the more viscous, the less friction and thus the less power needed. The two factors have a different functional range. When the solution is dilute, viscosity is the major factor. When the viscosity increases the friction factor becomes the main one and the power needed decreases due to the slippery bottom.

This combination of (at least) two factors makes this viscometer too difficult to calibrate for our experiments.

A capillary viscometer was used to measure the viscosity. The apparatus shown in Figure 22 is an example of one of many such instruments known. In such an experiment the time required for the meniscus to drop the distance between the lines etched at opposite ends of the top bulb is measured. This corresponds to the drainage of a fixed volume of liquid through a capillary of constant shape and volume. The weight of the liquid is the driving force for the flow, and the flow time is largely determined by the solution viscosity.

Three capillary viscometers with different diameters of the capillary were tried to check the method. The sample was 300.0 mg of polystyrene with different molecular weight in 10.0 ml of THF. Two groups of data are shown below:

Sample No.	THF	1	2	3	4	5	6	7
MW		3500	9200	11900	22000	30800	54850	68230
Mw/Mn		1.52	1.46	1.24	1.40	1.11	1.08	1.07
Time* (sec.) for L323/75#	71@	94	98	96	115	118	145	154
Time (sec.) for K830/100#	29	38	40	40	47	49	60	62

* the time required for the THF solution to flow through the capillary viscometer.
# the series No. of various capillary viscometer.
@ the time measured three times for every one, the error is 1 second.

The result does not show a regular relation between the solution viscosity measured and the molecular weight of polystyrene. This is probably due to the different polydispersities.

The above two methods are very fast to measure viscosity. This is important since the concentration of the anionic living chain can decrease due to impurities. In general the living concentration could keep constant for only half an hour. So the faster the measurement of the viscosity the better the method. But the main problem with the above two viscometers is the small variation of the viscosity with molecular weight. Viscosity of a polymer solution is a mixing function both of concentration and polymer molecular weight. So any error in concentration results in an error in the calculation of molecular weight from viscosity.

Another method to measure the absolute molecular weight directly and quickly was therefore necessary. The third method, used one GPC column with a measurement range from MW 3,000 to 60,000 of polystyrene, PL GEL 5μ, 10^3 Å, 1.5 ml/min flow rate of elution, UV Detector 214 nm. Under these conditions, the MW of polystyrene sample can be obtained in 5 minutes. The whole process from preparation of the GPC sample to getting the data takes about 7 to 8 minutes. This speed is fast enough for our purpose of measuring MW and the concentration of living polystyrene before adding in difulvene, the terminator.

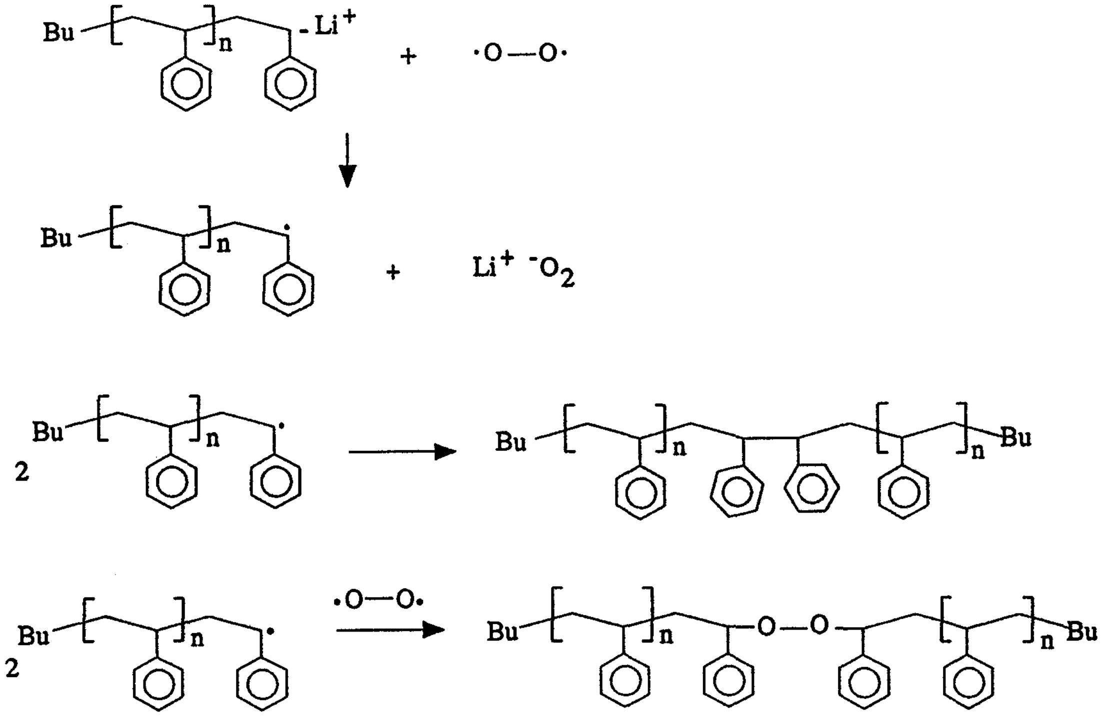
5. Preparation of GPC samples

When the 100 μl of living polymer solution sample was taken out from the flask by syringe, it was injected into 2 ml of THF containing three drops of trimethylchlorosilane or 1% MeOH under nitrogen. Even though these samples will be used in GPC and the kind of terminator used will not influence the GPC result, oxygen was found to be a problem. If there is some oxygen (air) inside the 2 ml of THF, it will oxidize the polymer anion very fast, and a small peak with double molecular weight would be there together with the main peak of polystyrene in GPC (see Figure 23 sample No. sl149-1 and sl150-1). In Figure 22 curve (a) corresponds to a sample (sl149-1) made by injecting 100 μl of living polystyrene into THF which is open to the air. Curve (b) corresponds to a sample made by injecting 100 μl of living sample (sl151-1) into THF under nitrogen flow.

Sample No.	Mn	Mp	Mw/Mn
sl149-1	24500	24900	1.10
sl151-1	22430	24000	1.05

The small peak with double molecular weight was possibly produced by oxidation of living chain. It can be seen that this oxidation broadened the distribution of molecular weight .

The possible reaction might be:



6. Summary of the development of the bench-top method

To develop an efficient method for bench-top living anionic polymerization take many attempts. Eventually polydispersities around 1.05 to 1.15 and controllable molecular weight were obtained. This is shown in Figure 24.

The bench-top method is not as good as a high vacuum line method which can produce a polydispersity of 1.03. However polymers terminated with a high percentage (> 90 %) functional group and predictable molecular weight can be obtained. This just what is needed for the research of a novel class of viscosity index improvers.

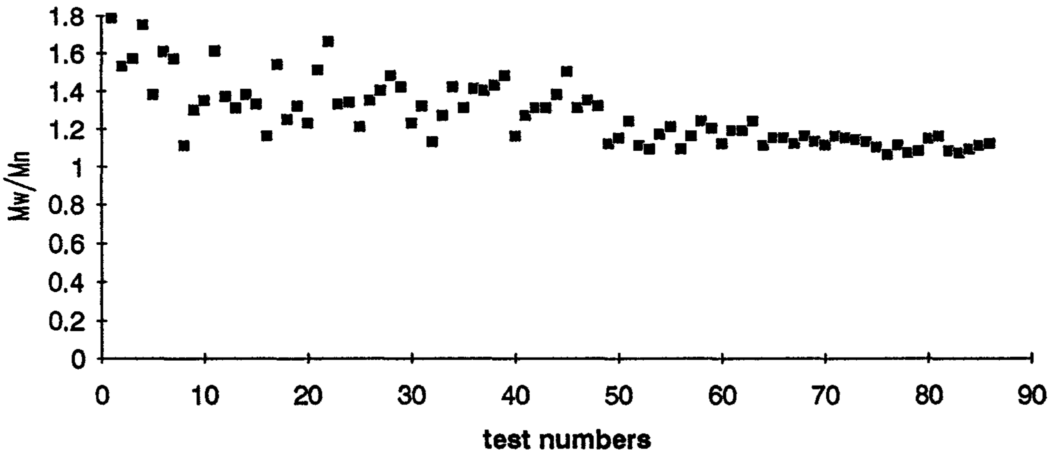


Figure 24. Relation between test numbers and polydispersities

The result that a high percentage (> 90 %) living chain can be obtained in this bench-top method is shown in the following Figure 25. After an anionic initiation step five times 0.5 ml styrene were added one by one, and a polystyrene sample was withdrawn after every 0.5 ml of styrene injection.

Amount of styrene (ml)	Mn of polystyrene	Increase of Mn	Mw/Mn
0.5	3550		1.24
1.0	6000	2440	1.11
1.5	9200	3200	1.15
2.0	11600	2400	1.15
2.5	13400	1900	1.12

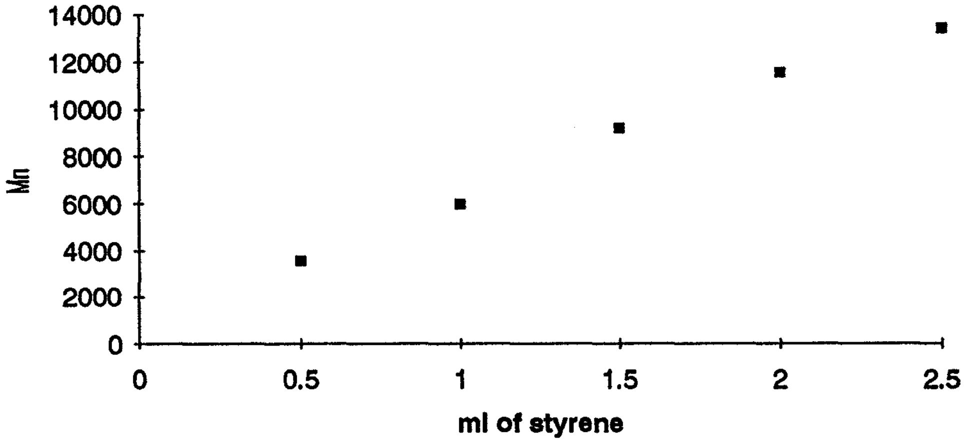
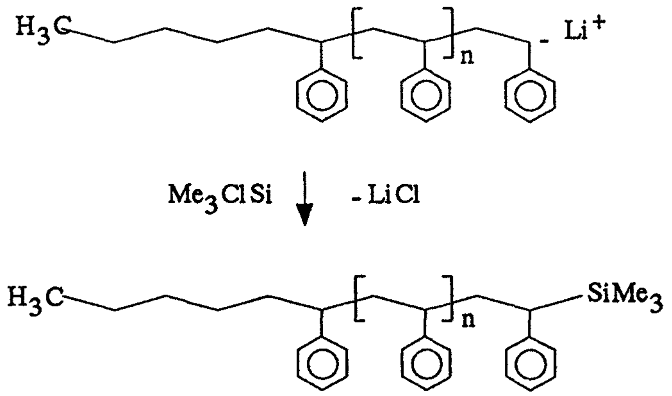


Figure 25. Relation between polystyrene MW and amount of styrene used

Figure 25. shows the plot of molecular weight versus amount of monomer added. The plot is almost linear, indicating the living character of this polymerization.

In another method to measure the percent living polymer trimethylchlorosilane is used to terminate the living polystyrene. ^{1}H NMR can then be used to measure the integration ratio of methyl protons on the Si end (protons I) to methyl protons on the butyl end (protons II) (see Figure 26). Polystyrene terminated with trimethylchlorosilane should contain three methyl protons on butyl end of the chain and nine methyl protons on the Si end of the chain. If all the living polystyrene chains are terminated with trimethylchlorosilane the integration ratio of protons I to protons II in ^{1}H NMR should be 1:3. If 50 % of living polystyrene chains are terminated by impurities and 50% by trimethylchlorosilane the ratio should be 1:1.5.

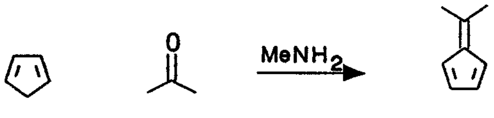


As well, the integral ratio of the methyl protons of the butyl group to the methylene protons of the polystyrene backbone can be used to calculate the MW of polystyrene.

Figure 26 shows part of a ^{1}H NMR spectrum and one polystyrene sample. The two overlapped peaks at 1.2 to 2.2 ppm correspond to the methulene and methine protons in the backbone of polystyrene. The small peak at 0.75 ppm is due to the three methyl protons on the butyl end of polystyrene. The ratio of these two integrations gives the molecular weight of 11420, close to the GPC valut for Mn of 12960 (sample No. sl057-2). Another small multiple peak around -0.2 ppm is due to the nine protons on silyl methyl groups at the other end of the polystyrene chain. The integration ratio of this peak to the peak at 0.8 ppm gives the living percent of 87 %.

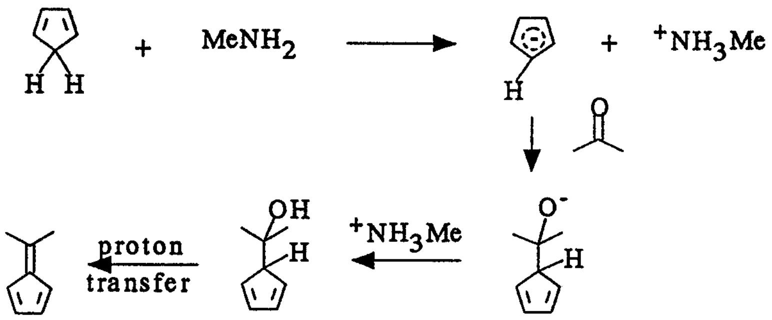
3.2 Synthesis of Fulvenes

1. 6,6'-dimethylfulvene (A)



(A)

In this reaction methylamine functioned as a base to produce cyclopentadienyl anion as intermediate:



(A) (B)

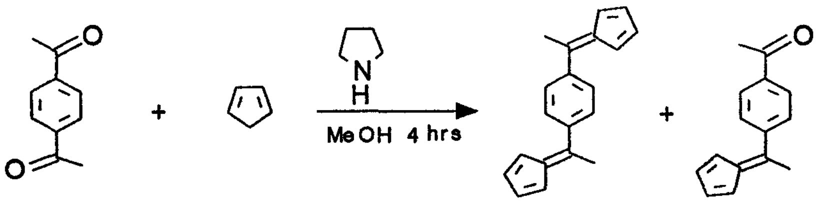
The alcohol (B) is a possible by-product.

In this project, the synthesis of this dimethyl fulvene was used to compare different methods for fulvene synthesis. Whike the process is simple, the yields were low. Since methylamine was used in 40% aqueous solution the reaction mixture formed two phases during the reaction. Especially in the case of water-insoluble ketones, the reactions were heterogeneous. This may have contributed to the low yields.

2. 1,4-di(6'-6'-dimethyl-fulvyl)-benzene (C)

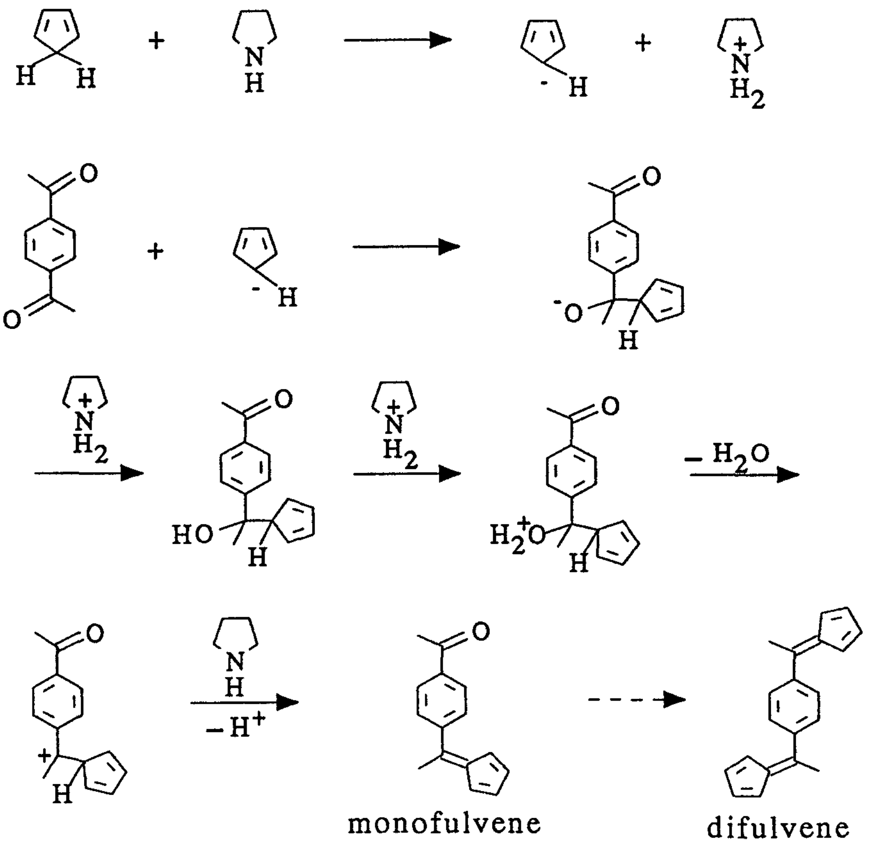
This is the main compound that was used as a functional terminator of living polystyrene in this thesis.

Pyrrolidine was used as a base in this reaction:



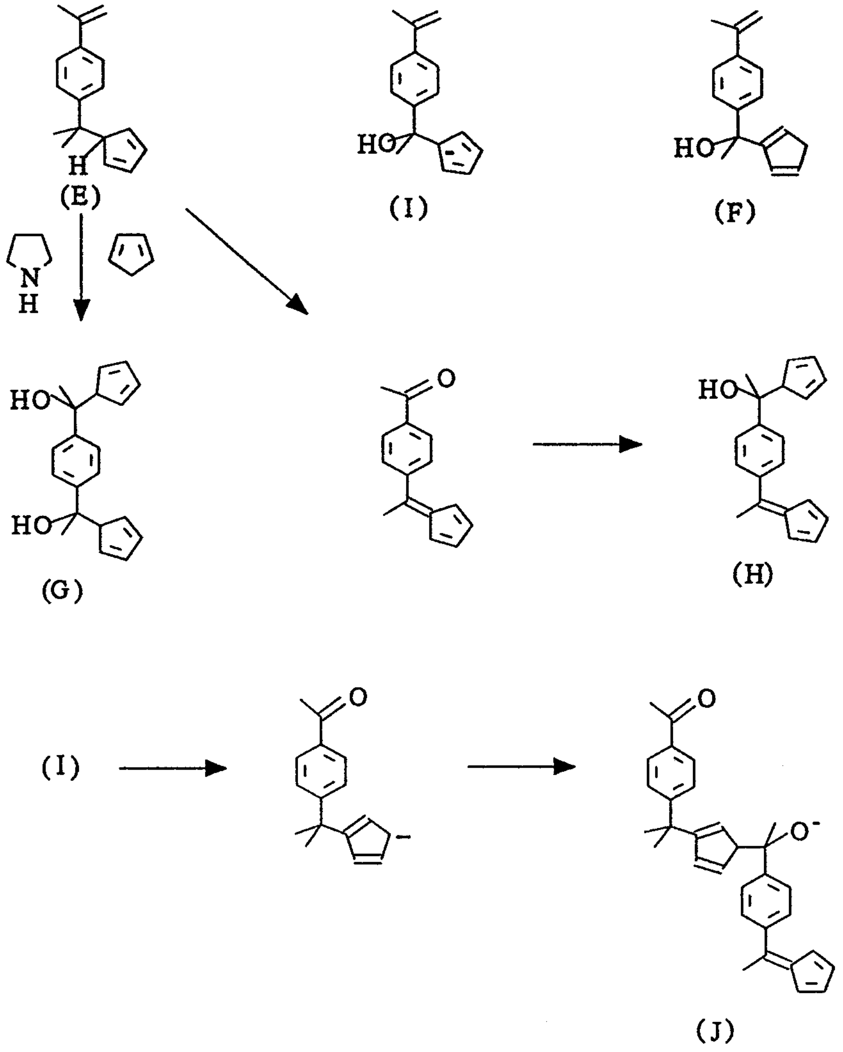
(C) (D)

In principle the synthesis of difulvene is a nucleophilic addition and elimination reaction. Pyrrolidine serves as proton transfer agent.



As well, and not shown here, pyrrolidine may activate the carbonyl compound through intermediate formation of the immonium cation.

The total yield of monofulvene and difulvene together is 40 %. There was some black and viscous substance left on the top of the column when column chromatography was used to separate these products. These are probably some fulvenes or oligomers with or without hydroxy substituent as listed like E, F, G, H, I, and J below, as well as some other sideproducts such as those derives from amine condensation (not shown).

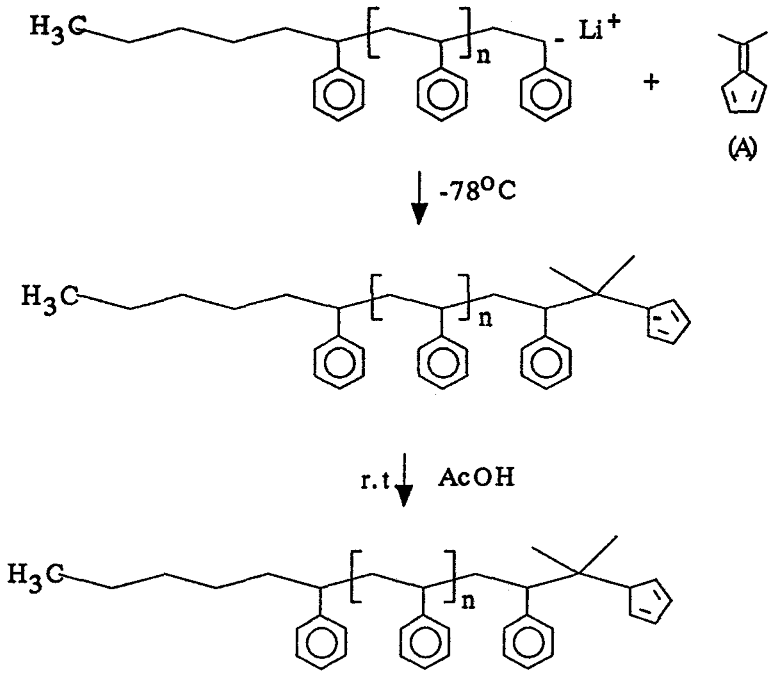


3.3 Polystyrene terminated with fulvene

When monofulvene is used as a terminator for living anionic polystyrene the resulting polymer will have a cyclopentadiene functional end.

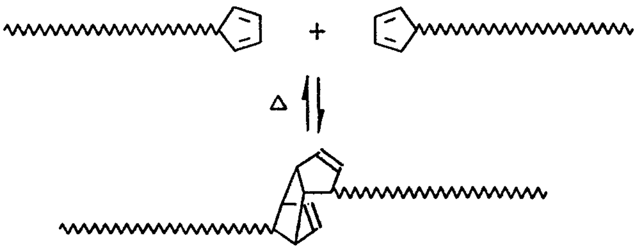
1. Polystyrene terminated with 6,6'-dimethylfulvene (polystyrene 1)

The termination reaction is



1

In the new polystyrene (1) there is one cyclopentadiene group at the end of the chain. Since cyclopentadiene easily dimerizes at 45°C and 20 % can dimerize in bulky state in three hours, it should also be possible for this reaction to occur in polystyrene (1) in a longer time. The reaction will be a Diels-Alder coupling of two polymer chain ends, and should lead to a doubling of the molecular weight.



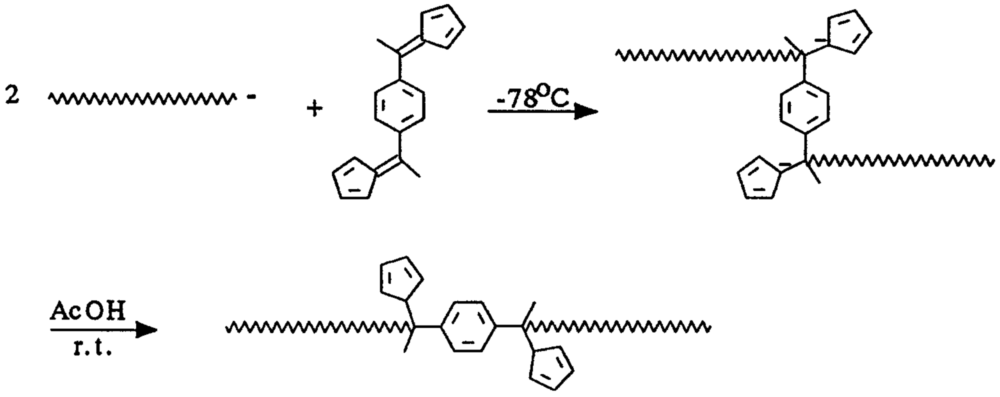
Howeverm no such reaction was observed. One reason is the solution is too dilute in cyclopentadiene groups even though it is fairly concentrated in polymer. Also the temperature is low. If the temperature is increased to 100°C or higher the reaction rate will increase. Another reason is the attachment to the polymer makes it difficult for the cyclopentadiene end groups to diffuse to meet each other, this reduced the mobility of the functional groups.

2. Polystyrene terminated with difulvene (polystyrene 2)

After this termination about 90% living polystyrene doubled their molecular weight and 10% remained with the original single molecular weight (see figure 12). Some samples and their results are listed below:

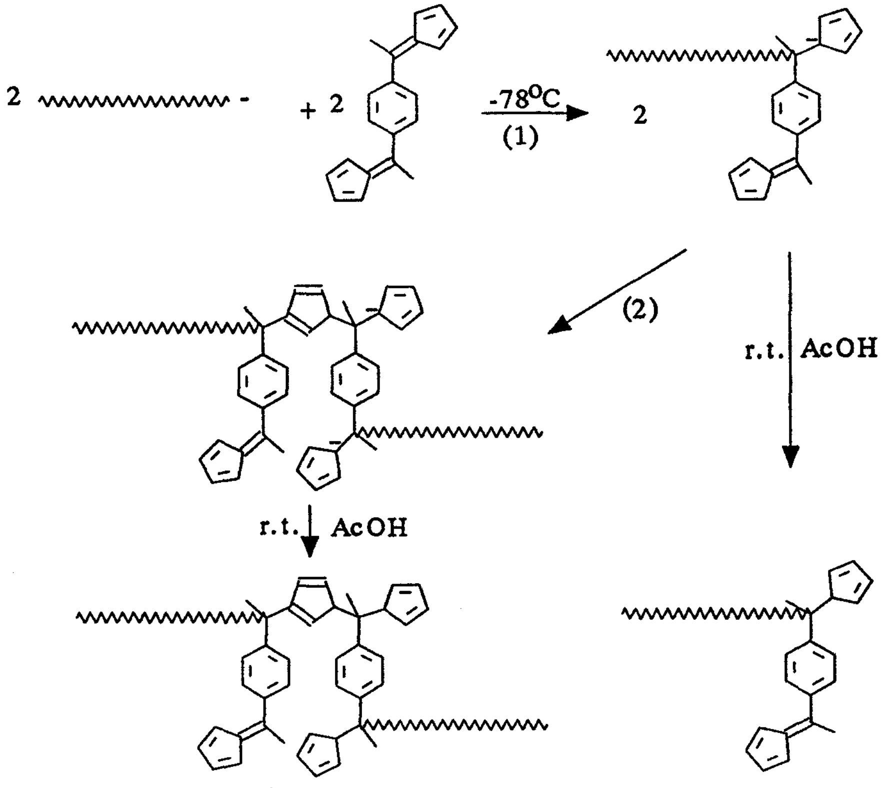
	before difulvene termination		after difulvene termination	
			peak 1(single)	peak 2(double)
sample No.	Mn ; Mp	Mw/Mn	Mn ; Mp	Mn ; Mp
sl169a	39350; 39320	1.07	39820; 39320	76780; 79010
sl169b	28400; 27890	1.09	27960; 27590	55650; 56290
sl169e	31120; 30280	1.12	28100; 28590	58350; 59830
sl165a	11650; 12110	1.06	11780; 12270	26000; 26260
sl165b	53650; 56290	1.06	53930; 54610	92580; 89590

1,4-di(6'-6'-methyl-fulvyl)-benzene (C) contains two fulvene groups. It was expected that one difulvene can therefore react with two living polystyrene chain to double the polystyrene molecular weight. The reaction was expected to happen like



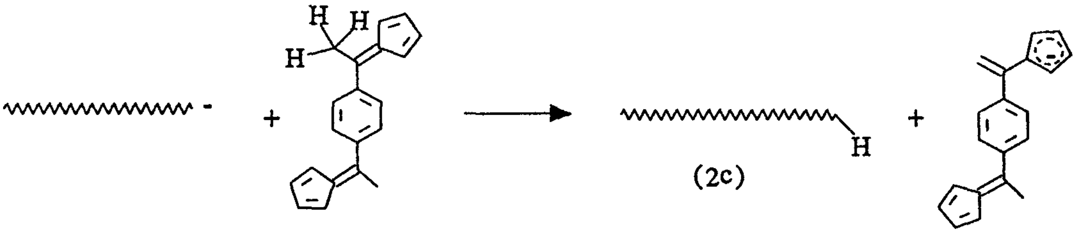
2

Since the final product has a light yellow color and some single molecular weight polystyrene remained, it is possible that the following reactions happened and some fulvene group is still left on the polymer. Polystyrene 2 would thus be a mixture including 2a and 2b shown below:



(2a) (2b)

Another possible component of polystyrene 2 might be a very small amount of dead polystyrene 2c :



Polystyrene 2c is the product of termination by proton transfer.

When one mole equivalent of difulvene (C) was used, all living polystyrene should became polymer (2b) if the reaction (1) is dorminant. But in the GPC result of the polystyrene after termination there are always still two peaks. The ratio of the double molecular weight peak to the original molecular weight peak varies from 55:45 to 90:10 in the best case.

In Figure 26, curve (a) is the molecular weight distribution (MWD) before the difulvene termination, the small peak at double Mn position is due to the oxidation by air when the living polystyrene was injected into a open vial for the sample preparation for GPC. Curve (b) was measured one hour after termiantion with difulvene (C). Curve (c) was measured four hours after termination. A relative decrease in the height of single MW peak and a relative increase in double MW peak with time can be observed.

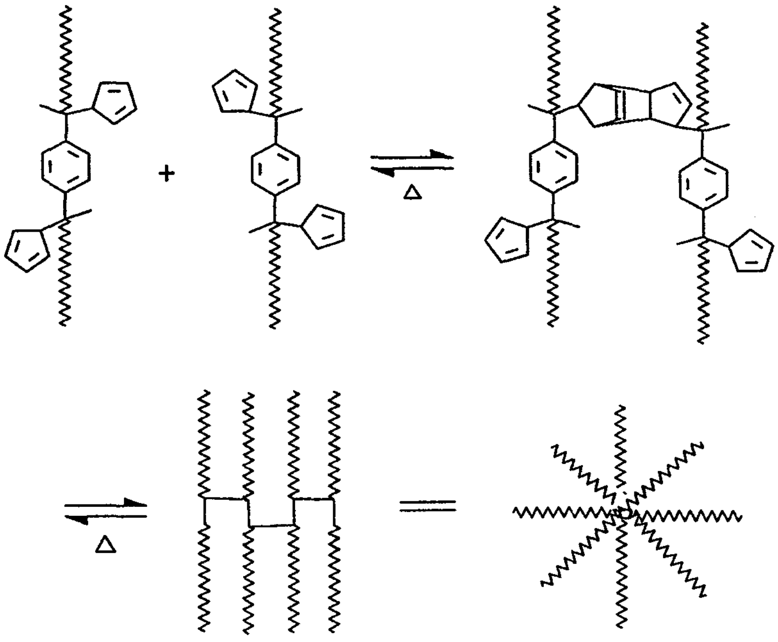
3.4 Chemistry of Polystyrene Terminated with Difulvene

Terminations on di or monofulvenes results in neutral polystyrene molecules with functional cyclopentadiene groups in the middle or at the end of polystyrene molecules.

1. Test for Retro- Diels-Alder reaction (polystyrene 3)

Cyclopentadiene monomer can undergo Diels-Alder coupling to form dicyclopentadiene. The reaction can be speeded up by heating. The reverse reaction happens when the temperature increases to 160°C.

The same reversible reaction was expected to happen in polystyrene having cyclopentadiene group at the chain center. This was the crucial purpose of this research. The reaction would be



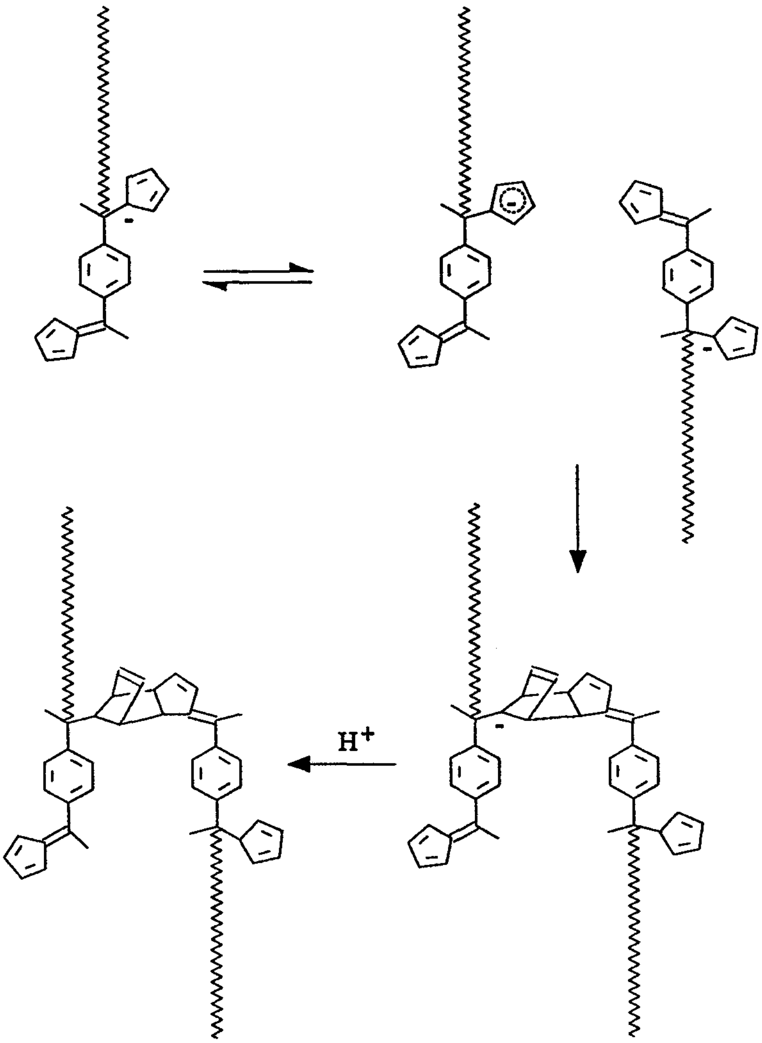
3

If Diels-Alder reaction happened according to the above path the molecular weight of the polymer would increase and a branched or star-shaped polymer would form. But during the heating of this polystyrene solution (see experimental 11.) there was no increase in molecular weight. On the contrary some polymer chains with double molecular weight cleaved to form molecules which have single molecular weight (Figure 13 sample No. sl173b,d). In Figure 13 curve (a) is the title polystyrene before heating, curve (b) is the polystyrene heated to 50°C for 24 hours while curve (c) corresponds to the polymer heated to 90°C for 24 hours. It can be seen that higher temperature caused more cleavage of the double molecular weight fraction.

The absence of molecular weight increase upon heating indicates that the above Diels-Alder reaction did not happen. The reasons are: 1) functional cyclopentadiene groups are at the center of the polymer chain, and not very mobile; 2) the concentration of the cyclopentadiene groups is too low to let them have the opportunity to meet each other; 3) steric hindrance.

Instead of molecular weight increase, a thermo-cleavage happened, polystyrene with double molecular weight broke into single molecular weight fraction. Polystyrene 2, 2a, 2b, 2c do not explain the phenomenon. There must be some thermo-reversible linkage between polystyrene chaina.

When living polystyrene anion attecked at the 6' position of difulvene, a intermediate (2") with a cyclopentadienylide anion formed. The lone pair of electrons functioned as electron releasing group and activate the two conjugate double bonds of cyclopentadienylide to function as diene in Diels-Alder reaction. Meanwhile the double bonds in neutral fulvene group also was activated as dienophile by the third double of fulvene. This assumption was demonstrated by AM1 calculation using HyperChem program. The result of this calculation is : with the same symmetry, the Homo orbital energy of the diene is -2.4 ev while the Lumo orbital energy of the dienophile is -0.9 ev. The very small energy difference made a easy Diels-Alder coupling at -78°C to form another possible termination product (2d), and it was reponsible for the thermo-cleavage in this case.

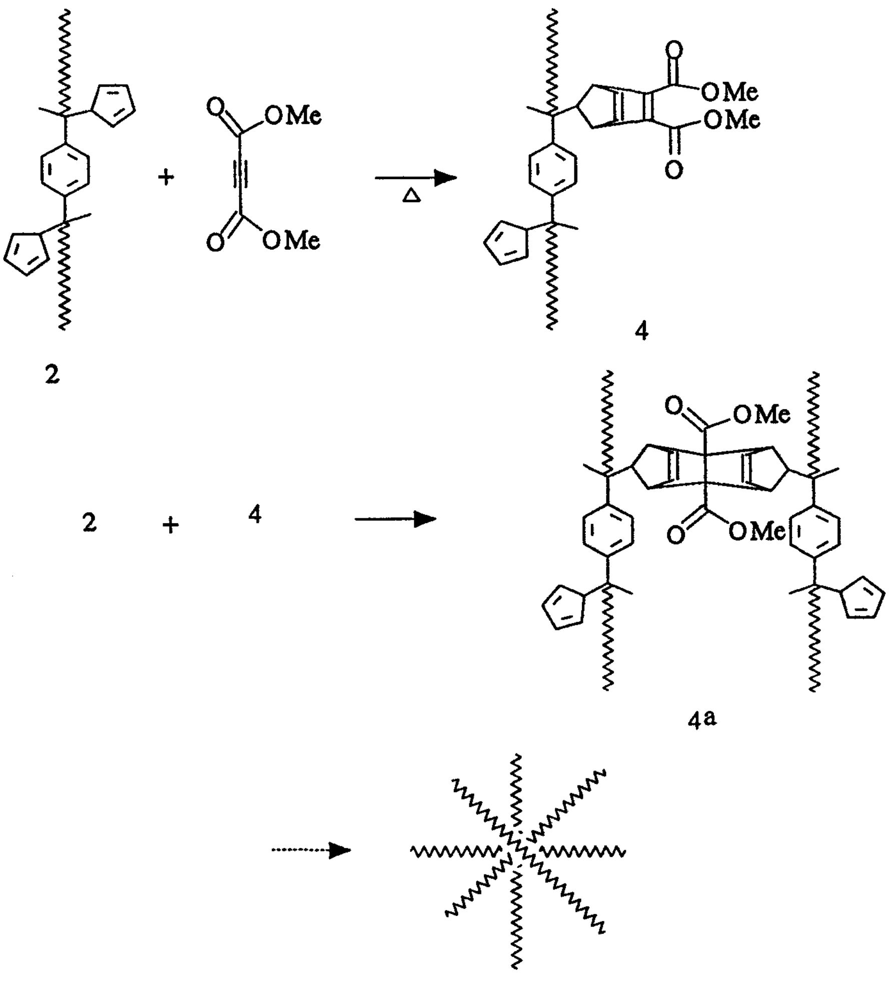


(2d)

2. Reaction between polystyrene 2 and dimethyl acetylenedicarboxylate (polystyrene 4)

In this case dimethyl acetylenedicarboxylate was used as a mobile small molecule to increase the rate of Diels-Alder coupling.

Dimethyl acetylenedicarboxylate is an extremely active dienophile in Diels-Alder reaction. It was tried here to function as a "glue" to connect polystyrene together:



If the above reactions could happen to polymer 2 (or 2a, 2b, 2c), a star-shaped polystyrene would be formed. But a decrease of molecular weight occured instead of an increase of molecular weight when polystyrene terminated with difulvene was mixed with dimethyl acetylenedicarboxylate and heated at 80°C for several days.

It appeared likely that the reaction just stopped at polymer 4. The triple bond in dimethyl acetylenedicarboxylate changed to double bond and this new double bond was not active enough to continue the Diels-Alder reaction with another cyclopentadiene group.

To prove this assumption, an excess amount of dimethyl acetylenedicarboxylate was reacted with polystyrene 2 (experimental 12). After 3 hours the yellow color of the original polymer solution had disappeared. The new polymer had multiple peaks at 3.82

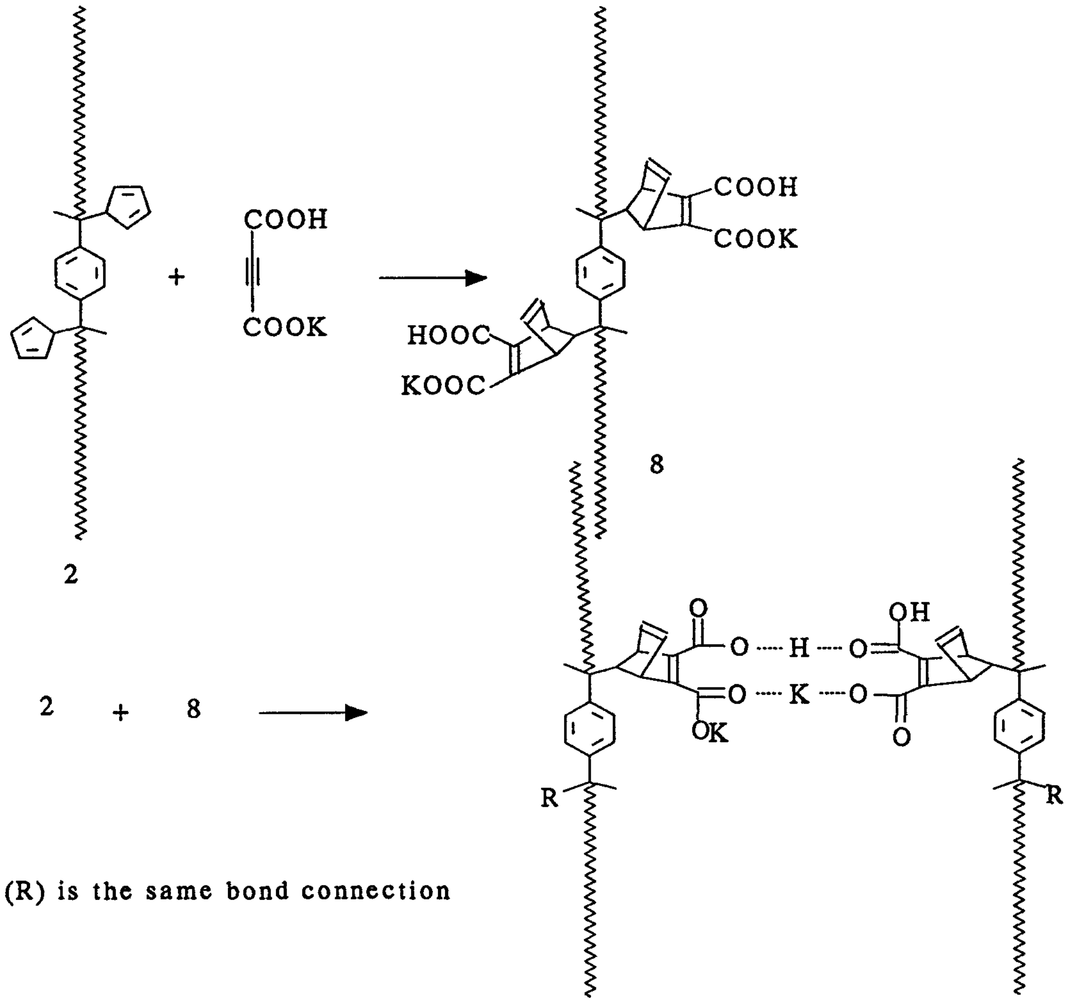
ppm which is the position of methoxy group in ^1H NMR (see Figure 14 sample No. sl175b, sl165a). In Figure 14 curve 1 is before the reaction and curve 2 is after the reaction. However the carbonyl group didn't show up in ^{13}C NMR, this group is too dilute and it has less intensity and longer relaxation time.

The carbonyl group, however, showed up in the FTIR (see Figure 15). A polystyrene background spectrum has been substracted from both FTIR spectra shown here.The top curve is the IR spectrum of the title polystyrene before the reaction with dimethyl acetylenedicarboxylate and the bottom curve is after the reaction. The carbonyl stretch vibration absorbance can be seen here at 1700 λ^{-1}. The broad peak around 3400 λ^{-1} is due to the absorbance of KBr, the supporting material. This polymer likely is the product of polystyrene 2 after Diels-Alder coupling of both cyclopentadienes.

4. Diels-Alder reaction catalized by Lewis acid, aluminum chloride

When aluminum chloride was used in the reaction between polystyrene 2 and dimethyl acetylenedicarboxylate, a more intense carbonyl group appeared in the FTIR spectrum (see Figure 15, the bottom curve), so a higher yield of Diels-Alder coupling might be the result of the catalyst.

Monopotassium acetylenedicarboxylic acid was used instead of dimethyl acetylenedicarboxylate. It may form hydrogen bonds or ionic bonds to aggregate polymer chains together like:



(R) is the same bond connection

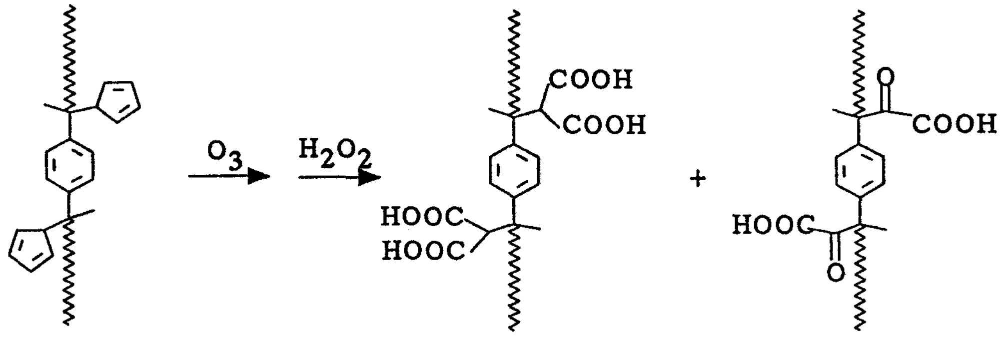
If the above coupling happened a star-shaped polymer would be formed by the hydrogen bond or ionic bond connection. But no viscosity increase was observed in capillary viscosity measurements. Such functional groups at the polymer center do however offer the possibility of covalent coupling, i.e. through ester formation with ethylene glycol.

5. Ozonolysis of the cyclopentadiene group of polystyrene terminated with fulvene can be easily achieved with an ozone generator. When pure oxygen flows through an electrical discharge, oxygen accepts the electrical energy and changes to ozone.

$$3\,O_2 \xrightarrow[\text{discharge}]{\text{silent electrical}} 2\,O_3$$

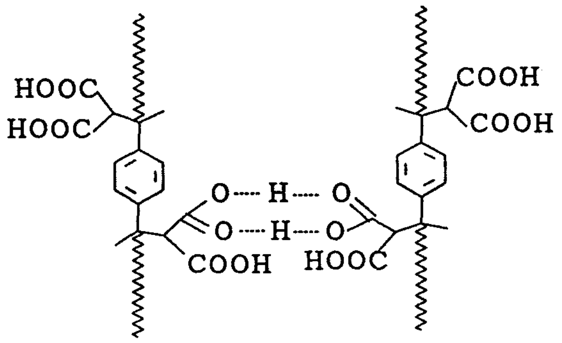
At -78°C, when ozone was bulbbled through the THF solution of polystyrene (2) with cyclopentadiene group, the yellow color of the polymer changed to clear in just a few seconds. The clear THF solution was stable under ozone flow for about one hour. A longer ozone flow will cleave the polystyrene backbone.

Ozonolysis of the cyclopentadiene group should oxidize the double bond and form carboxylic acid groups. The reaction is



10 10'

If polymer (10) was formed a possible increase of viscosity might be observed in nonpolar solvent since the hydrogen bond between acid groups can aggregate polymer molecules together as shown below:



10a

In the extreme case, a star-shaped polymer with a weak bond (hydrogen bond) linkage would form. However this was not observed in the GPC, even a small change in viscosity of a benzene solution of the polymer (10) in the capillary viscometer.

The carboxylic acid group in polymer (10) was not observed in both ^1H and ^{13}C NMR. In ^1H NMR the OH group might be overlapped by the broad peaks of polystyrene. In ^{13}C NMR the carbonyl group might be too weak to be observed.

In IR (see Figure 17, bottom curve), a sharp peak at 1600 λ^{-1} which is a typical carbonyl absorbance in carboxylic acid. The broad OH absorbance is difficult to see due to the same absorbance from KBr.

When using methylene chloride as solvent for ozonolysis, a green color and viscous cloudy solution like a gel formed at -78°C. Also methylene chloride solvent itself changed color during ozone bubbling. The chlorine atoms in methylene chloride might be easily removed out as radicals by ozone and the chlorine-radical can crosslink the polystyrene.

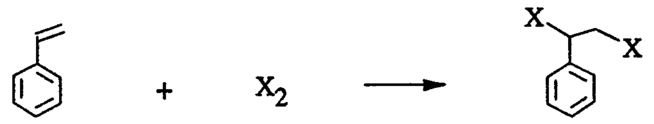
In IR measurement of the above ozonolysis product (see Figure 17, the middle curve) there is a broad multiple peak around 1700 λ^{-1}. This peak is probably an absorbance of aldehyde carbonyl group.

The crosslink reaction was proved by GPC which shows a broadening of molecular weight of polystyrene (see Figure 18) indicating some radical coupling between two polymer chains.

6. Bromination and Iodination of cyclopentadiene and styrene

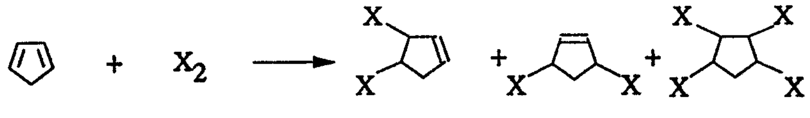
These experiments were done to compare with the bromination and iodinization of polystyrene (2) terminated with difulvene.

When bromine was added to styrene monomer, the red color of bromine rapidly changed to clear. When iodine was used in this case, iodine's color disappeared more slowly. So these reactions are typical addition reactions.



X = Br, I

When Br_2 and I_2 solutions were introduced into neat cyclopentadiene, similar addition reactions were expected:

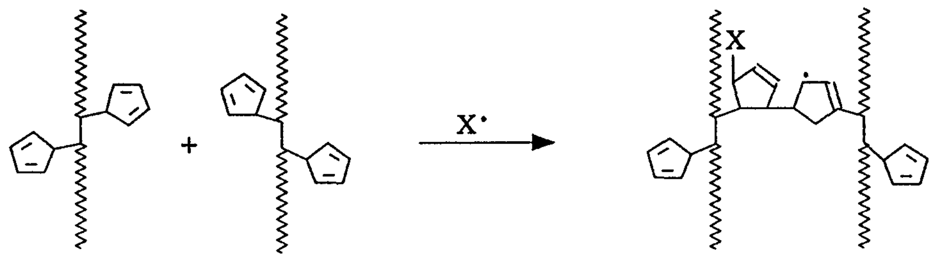


X = Br, I

However no addition happened. Cyclopentadiene has two conjugate double bonds and they are relatively stable to bromination and iodination. This gave bromine and iodine enough time to catalyze radical polymerization, initiated by light radiation, as well as cationic polymerization.

7. Bromination and iodination of polystyrene terminated with difulvene

Since bromine and iodine in the presence of light can initiate a radical polymerization of cyclopentadiene, it is possible to use this result in polystyrene terminated with difulvene which has cyclopentadiene group at the center of molecule chain. If such kind of light initiated radical polymerization can occur a star-shaped polymer can be obtained following the reaction shown below by a radical connection:

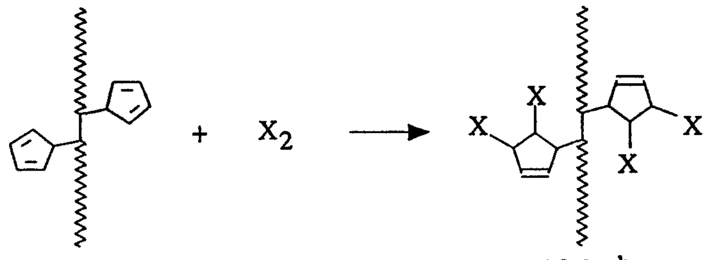


When iodine was introduced into the THF solution of polystyrene, the brown color of iodine did not change in several days. The solution didn't become viscous. In the GPC the molecular weight distribution was the same as it was before the reaction. So there was no radical coupling.

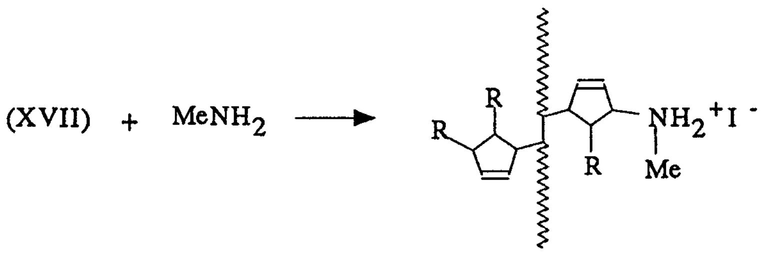
When bromine was added to the polystyrene solution, the brown red color became light yellow after one hour. In the GPC no change in molecular weight distribution was observed.

The radical or cationic coupling failed in both cases, probably due to too low concentration of functional groups.

It is possible that bromine or iodine addition happened to the cyclopentadiene group in a polystyrene molecule. To check this assumption, methylamine was used to substitute halogen atoms by amine.



13 a, b

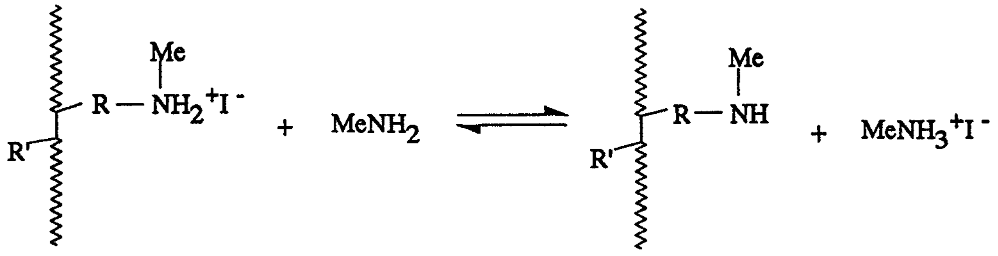


(R = $MeNH_2{}^+I^-$)

14

If polymer (13a, 13b) was the result of halogenation polymer, polystyrene (14) will form when methylamine is added.

In this case the ammonium ion formed can be partially deprotonated by the methylamine starting material to form polymer (14a, 14b):

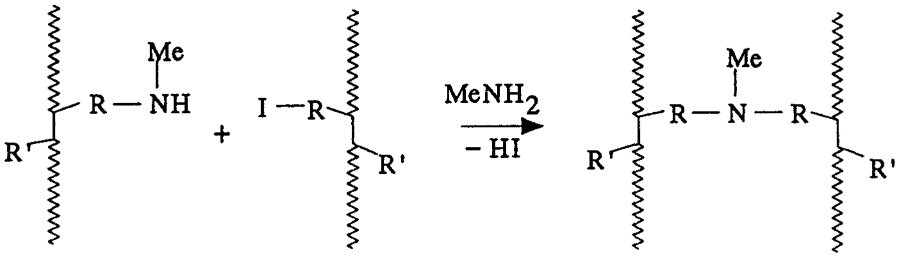


(R', R = cyclopentadiene ammonium salt) 14 a,b

In a competing reaction, methylamine could act as base to eliminate hydrogen bromide. A mixture of products is likely to result.

To check the possibility of the existence of polymer (13a, 13b) ^1H NMR was used. A small peak which might be the chemical shift of methyl group on nitrogen atom appeared around 2.4 ppm (see Figure 19).

Since the resulting amine (14a, 14b) is also a good nucleophile it may react with polymer (13a, 13b) to form a new ammonium ion. This ammonium ion can then be deprotonated by methylamine and form branched polymer (15) and then a star-shaped polymer.



14 a,b 13 a,b 15

In this type of reaction iodine substituted polymer will be more reactive to methylamine since iodine is a better living group. For bromine this reaction may need longer time.

However in the GPC of the above sample there was no increase in molecular weight both in bromo-substituted or iodo-substituted polystyrene.

Iodine undergoes addition to double bond with difficulty, especially to two conjugated double bonds. This was proved by experiment 18. In this experiment there was no change in color. So there was little polymer (13b) which has an iodine atom. This might be one reason in this case that polymer (15) was not observed.

Bromine did add to polystyrene terminated with difulvene in experiment 18. Bromine adds easier than iodine in the reaction with double bonds. So there could be more polymer (13a) with bromine atoms. But since bromine is not a good leaving group, bromine polymer needs longer time to undergo the substitution reaction with methylamine.

Conclusions

1. A bench-top method for living anionic polymerization has been developed and tested in many different aspects. Polydispersities between 1.05 to 1.15 can be obtained and the molecular weight of polymer can be controlled. The living percent can be as high as 90%.

2. A new difulvene, 1,4-(6'-6'-methyl-fulvyl)-benzene, has been synthesized and fully characterized.

3. The termination of living polystyrene with the above difulvene was then practiced. The molecular weight of the polymer was doubled by the termination. This new functionalized polystyrene has cyclopentadiene groups in the middle of polymer chain.

4. The cyclopentadiene groups were converted into other functional groups by ozonolysis of double bonds, Diels-Alder reaction between the cyclopentadiene groups and dimethyl acetylenedicarboxylate, and halogenation of the cyclopentadiene groups. An amine of the polymer after halogenation was also prepared.

Future Work

1. Go back to vacuum line. Under 10^{-6} mmHg vacuum and flaming, moisture, air and organic impurities can be removed completely so that the living polystyrene anion will have a longer lifetime and the polymer can have a narrower polydispersity.

2. Polystyrene with shorter chain length can be tested. In this way the concentration of functional groups on molecule chain can be relatively higher, and more mobile. This gives more opportunity for the occurance of Diels-Alder and other reactions of these functional groups.

3. Sec-BuLi initiator and benzene or toluene can be tried. Sec-BuLi is a better initiator than n-BuLi both in theory and in practice since the sec-butyl anion is a less aggregated and stable anion. Benzene is a non-polar solvent. Benzene also can decrease the propagation rate to make the anionic polymerization possible at room temperature.

4. A deuterated fulvene functional group can be tested.

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Appendix

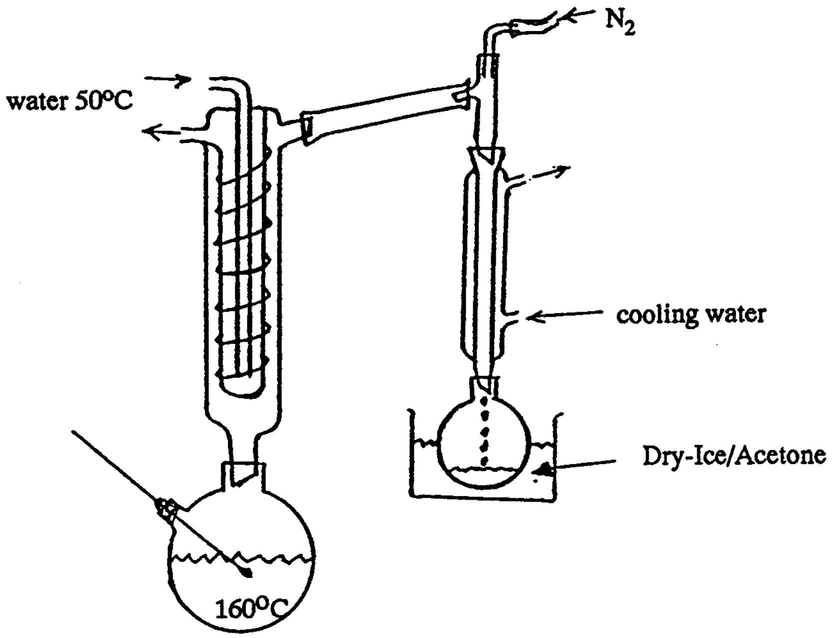

Figure 5. Apparatus for Pyrolysis of Dicyclopentadiene

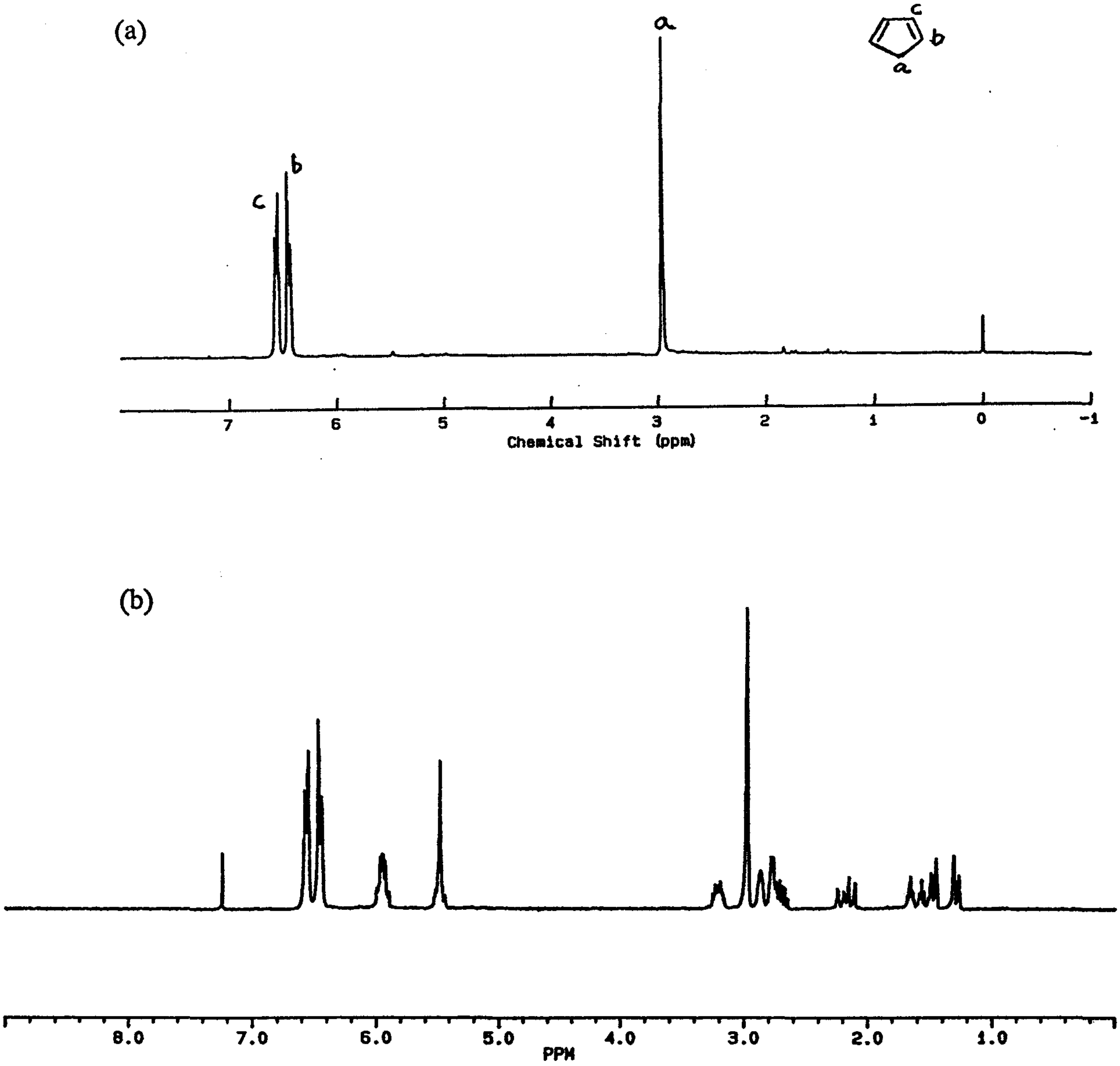

Figure 6. (a) ^{1}H NMR of cyclopentadiene monomer
(b) ^{1}H NMR of cyclopentadiene after 24 hours at room temperature

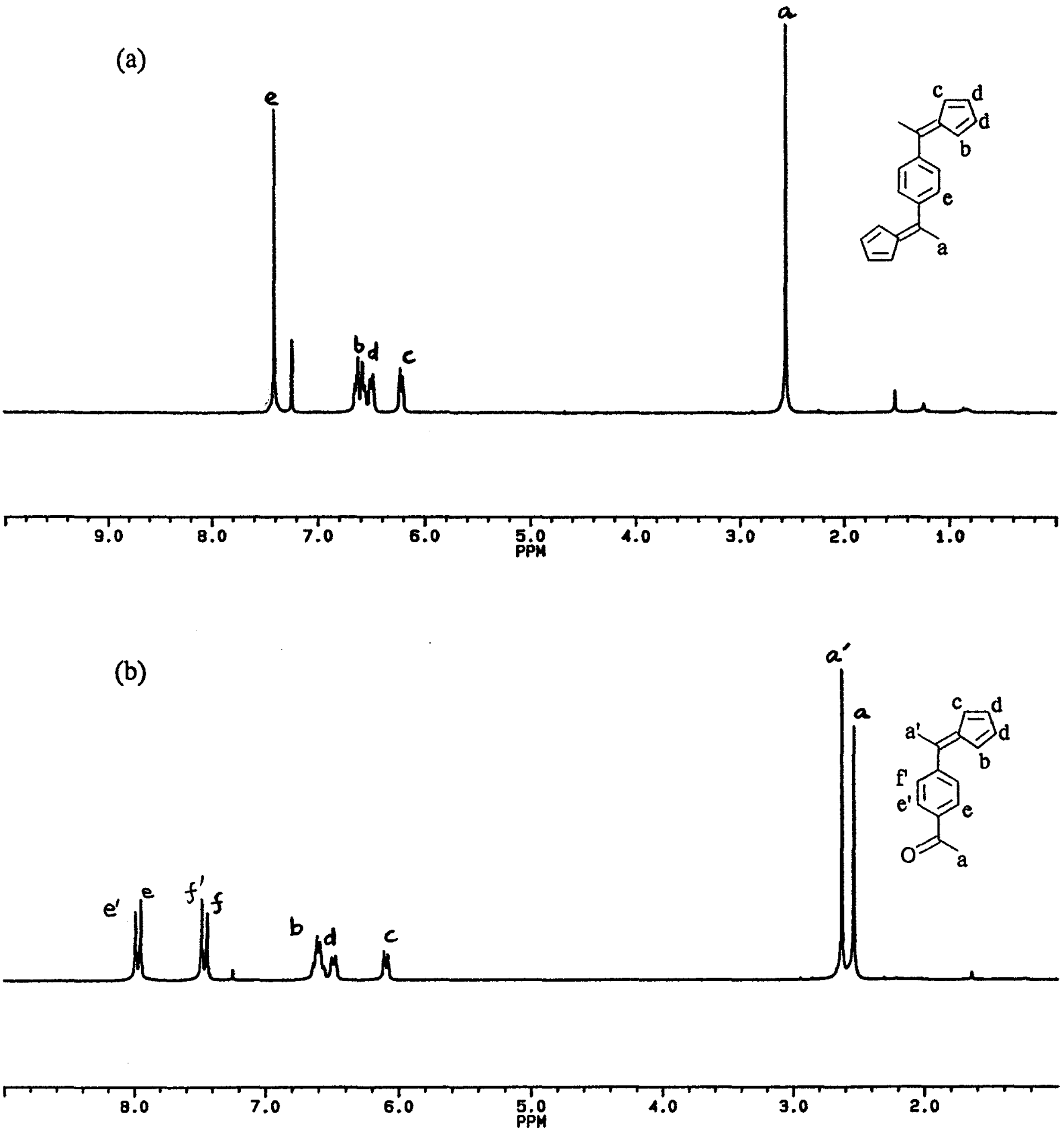

Figure 7. (a) ^{1}H NMR of 1,4-di(6'-6'-methyl-fulvyl)-benzene
(b) ^{1}H NMR of 1-(6'-methyl-fulvyl)-4-acetylbenzene

(c)

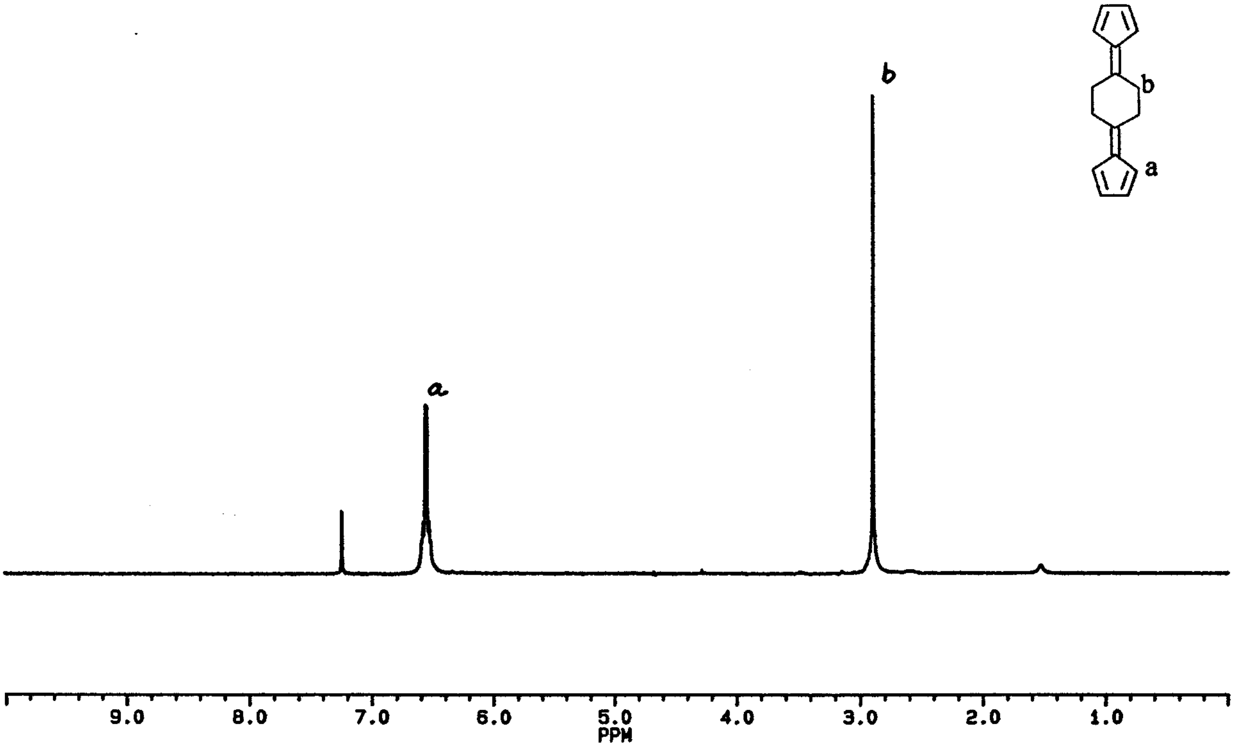

Figure7. (c) ^{1}H NMR of 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane

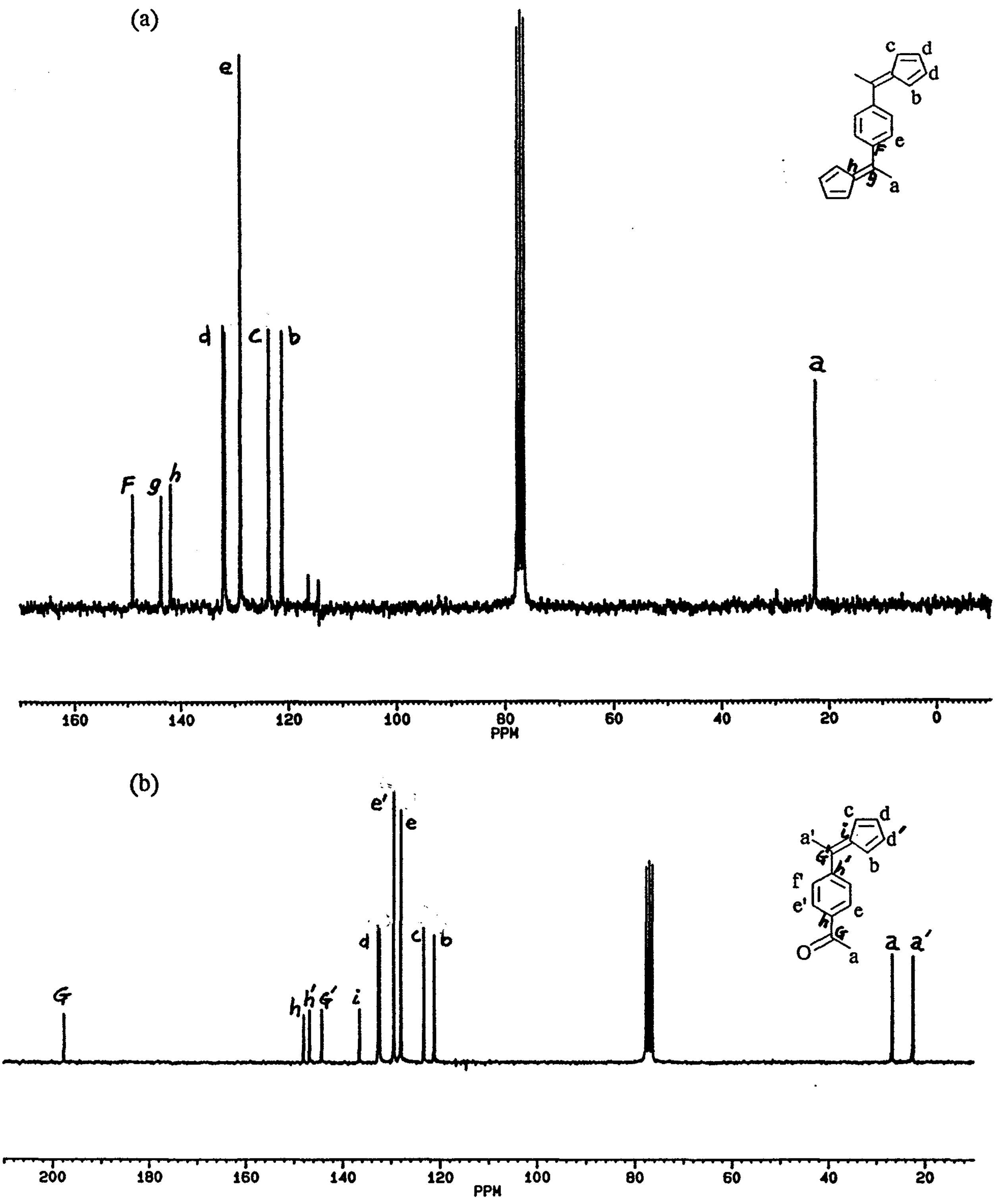

Figure 8. (a) ^{13}C NMR of 1,4-di(6'-6'-methyl-fulvyl)-benzene
(b) ^{13}C NMR of 1-(6'-methyl-fulvyl)-4-acetylbenzene

(c)

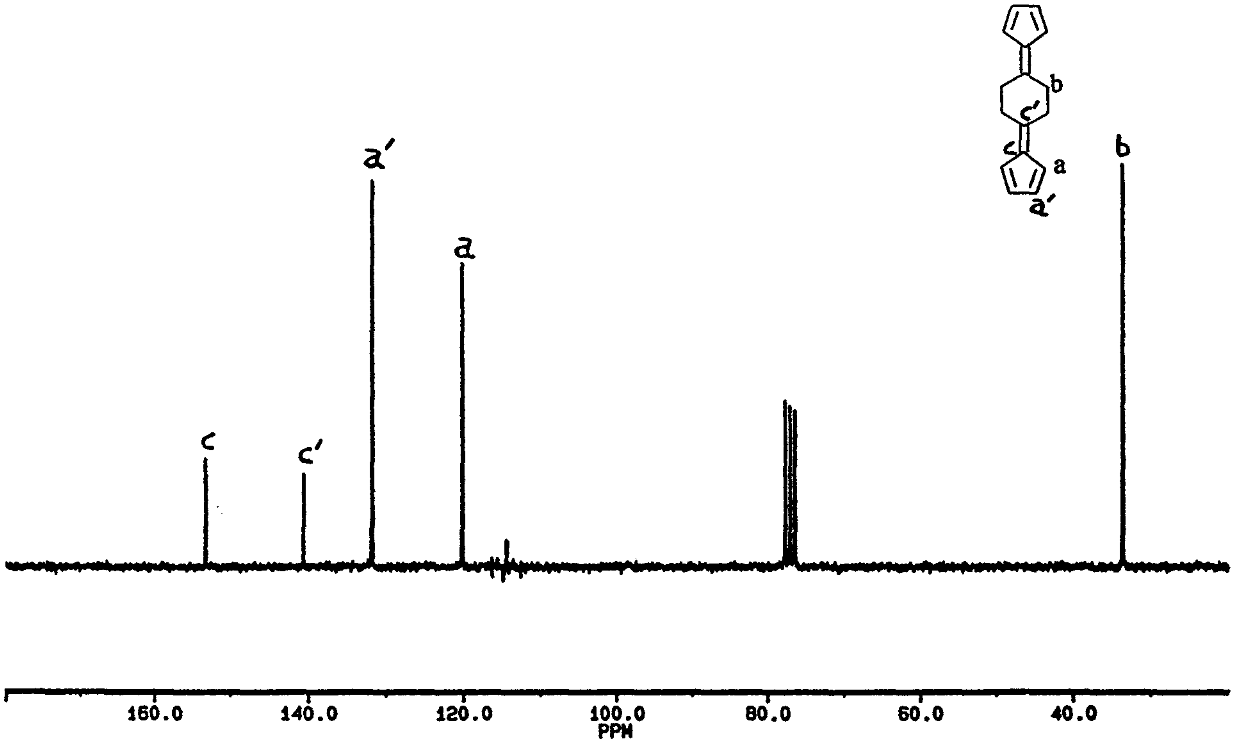

Figure8. (c) ^{13}C NMR of 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane

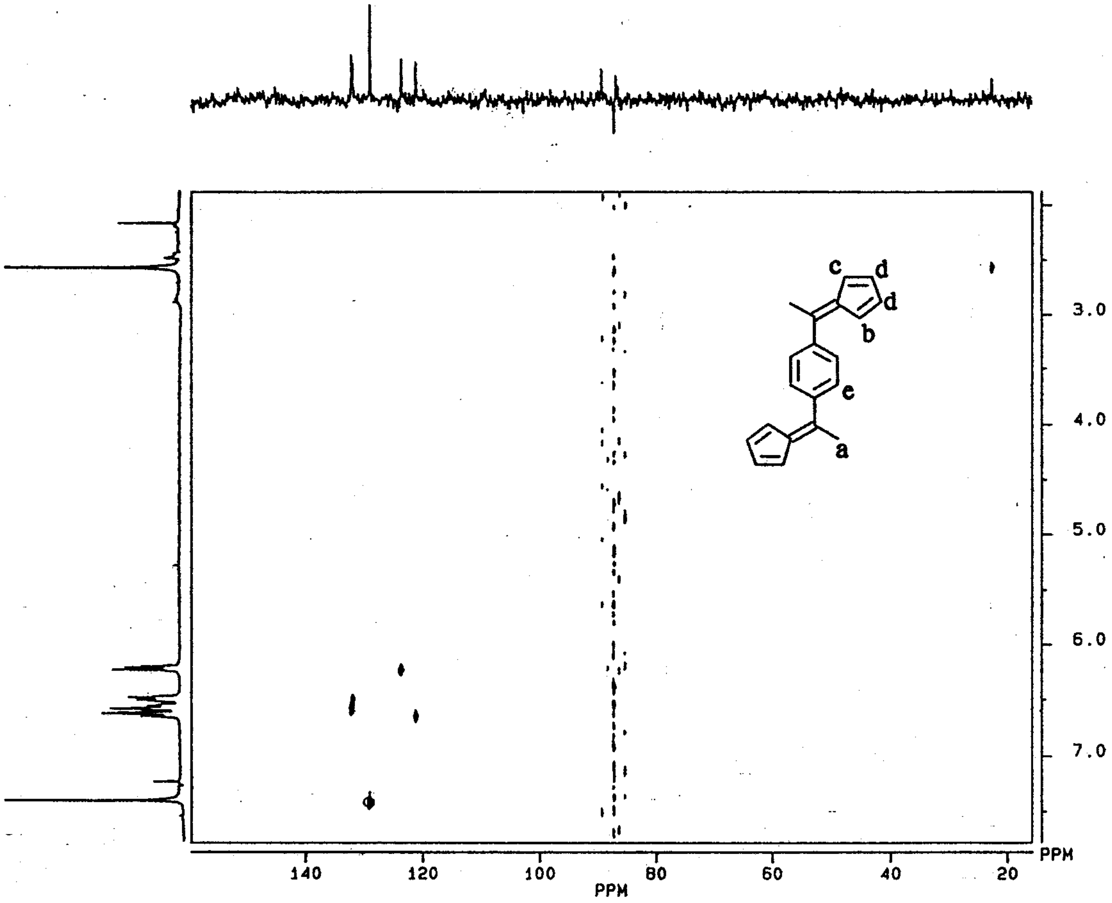

Figure9a. 2-D ^1H-^{13}C shift correlation NMR spectrum of 1,4-di(6'-6'-methyl-fulvyl)-benzene

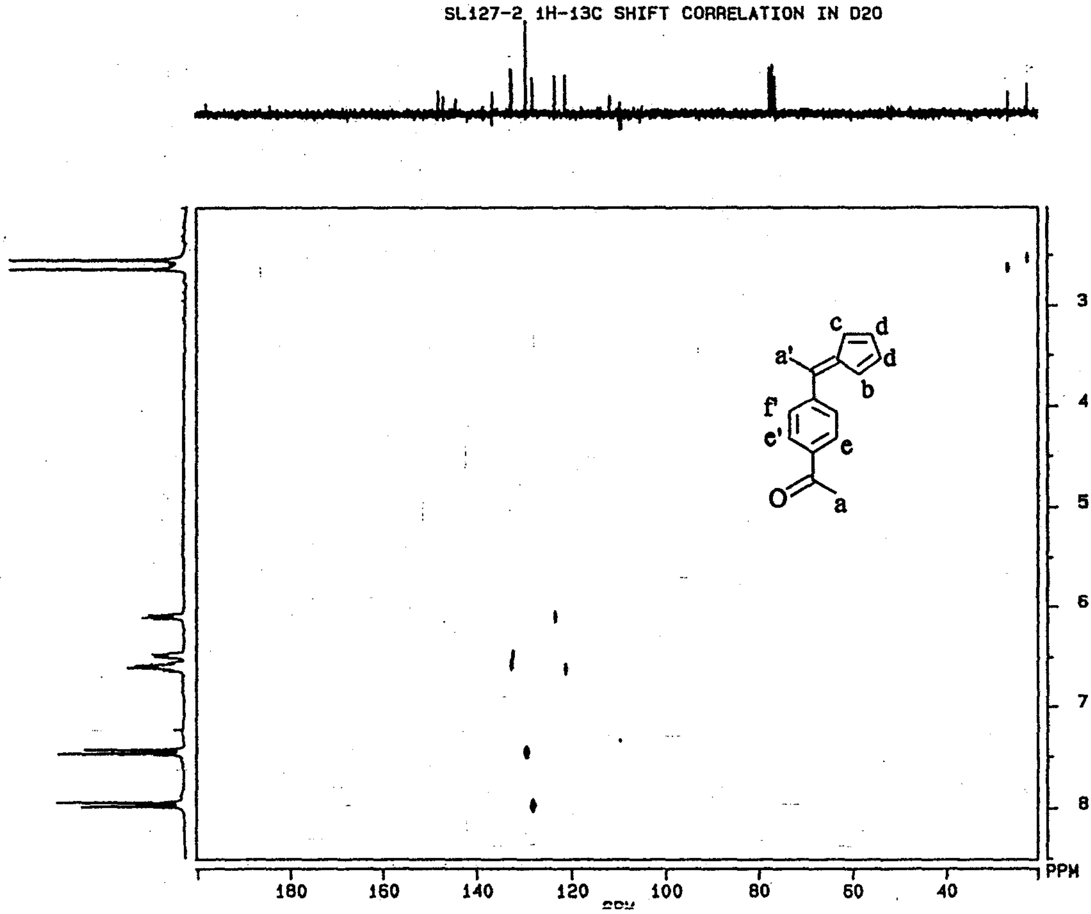

Figure9b. 2-D ^{1}H-^{13}C shift correlation NMR spectrum of 1-(6'-methyl-fulvyl)-4-acetylbenzene

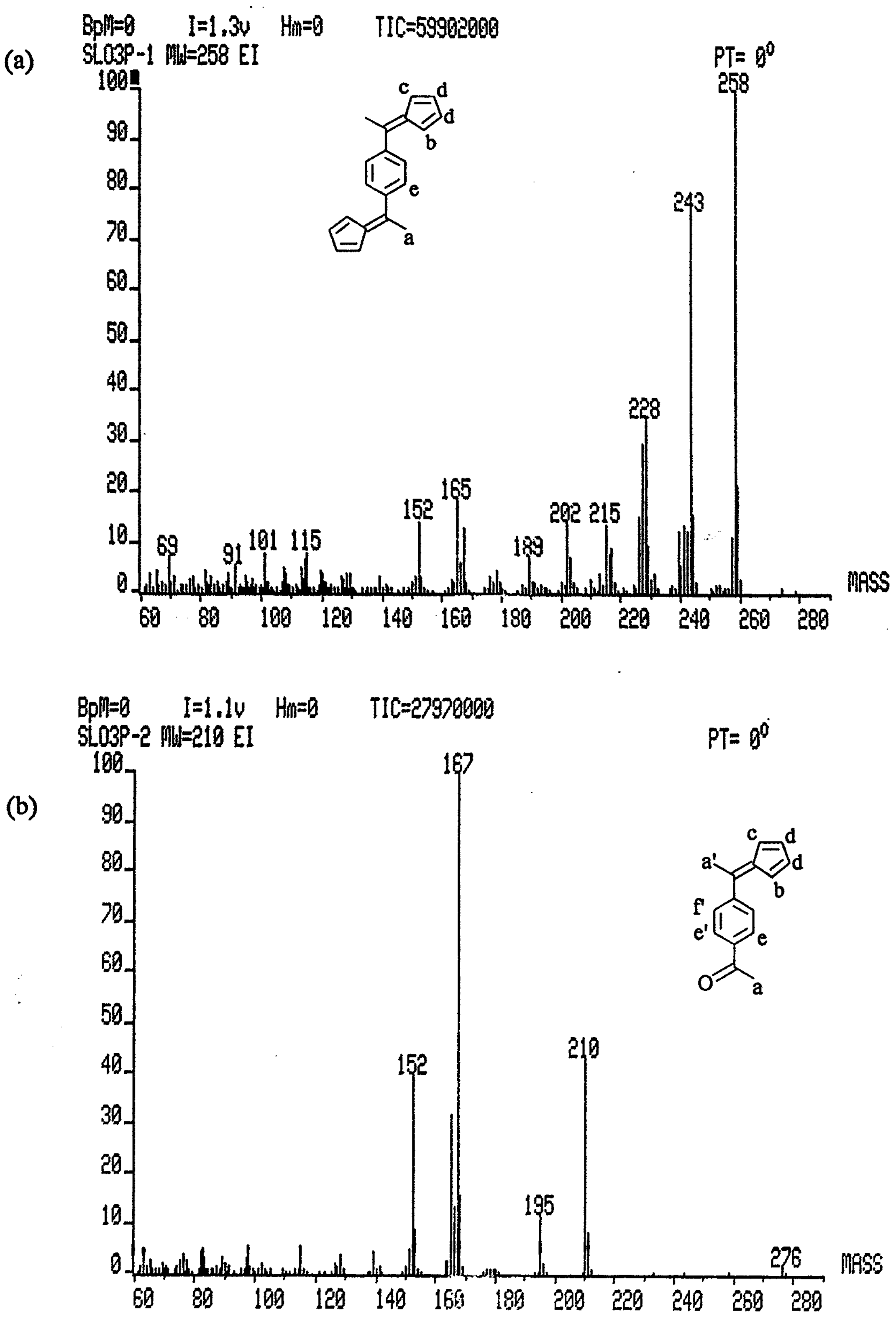

Figure 10. (a) Mass spectrum of 1,4-di(6'-6'-methyl-fulvyl)-benzene
(b) Mass spectrum of 1-(6'-methyl-fulvyl)-4-acetylbenzene

(c)

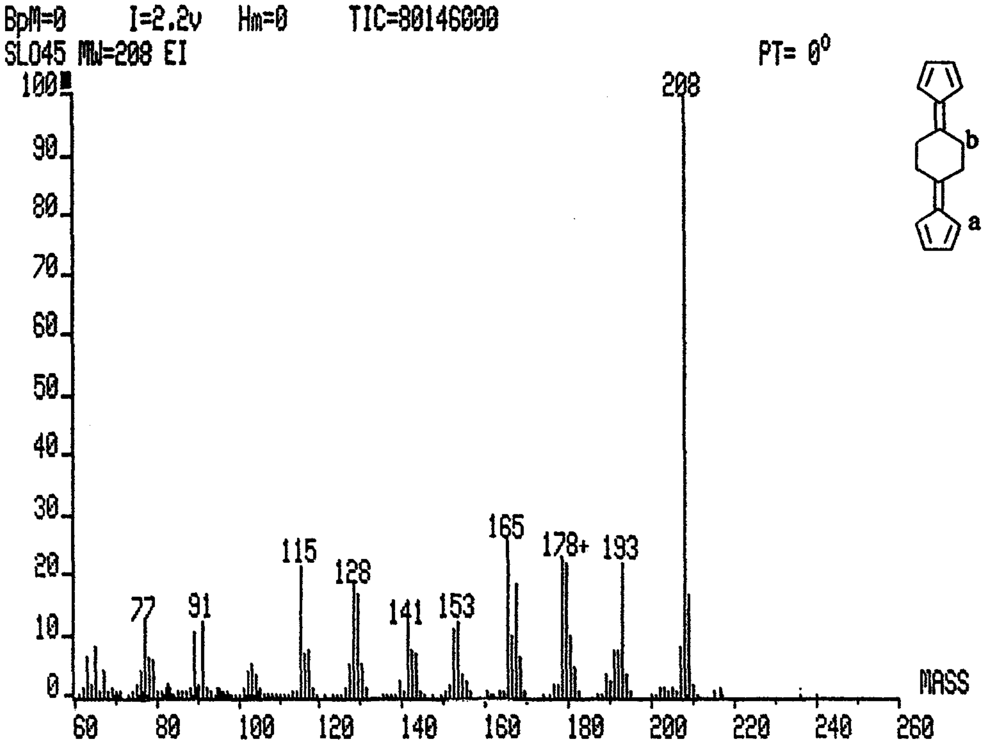

Figure10(c). Mass spectrum of 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane

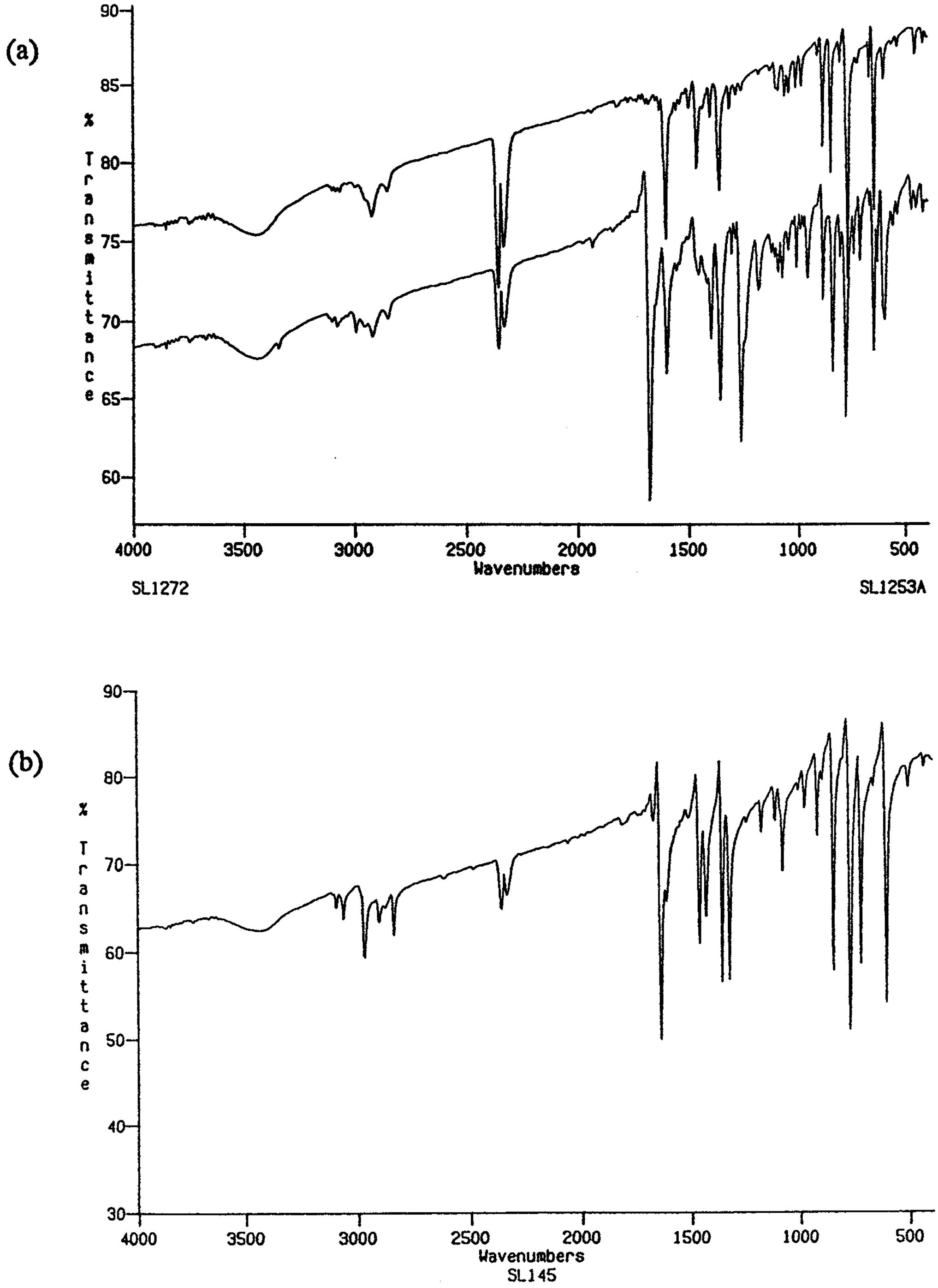

Figure 11. (a) Top curve : FTIR spectrum of 1,4-di(6'-6'-methyl-fulvyl)-benzene
Bottom curve : FTIR spectrum of 1-(6'-methyl-fulvyl)-4-acetylbenzene
(b) FTIR spectrum of 1,4-bis(2,4-cyclopentadiene-1-ylidene)cyclohexane

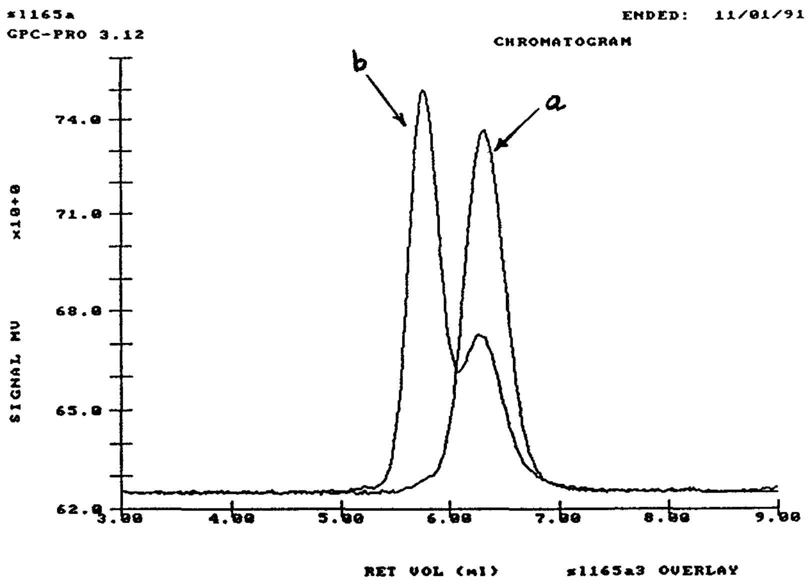

Figure 12. GPC chromatography of polystyrene
Curve (a) : living polystyrene MWD before difulvene termination (Mp 12,270)
Curve (b) : polystyrene MWD after difulvene termination (Mp 26,260)

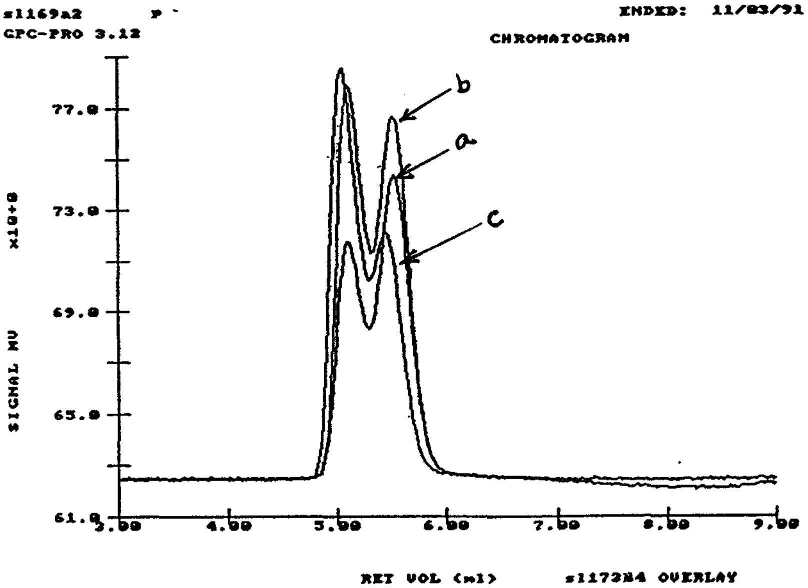

Figure 13. GPC chromatography of Diels-Alder test reaction of polystyrene
Curve (a) : polystyrene MWD before heating
Curve (b) : polystyrene MWD after heating 24 hrs at 45°C
Curve (c) : polystyrene MWD after heating 24 hrs at 90°C

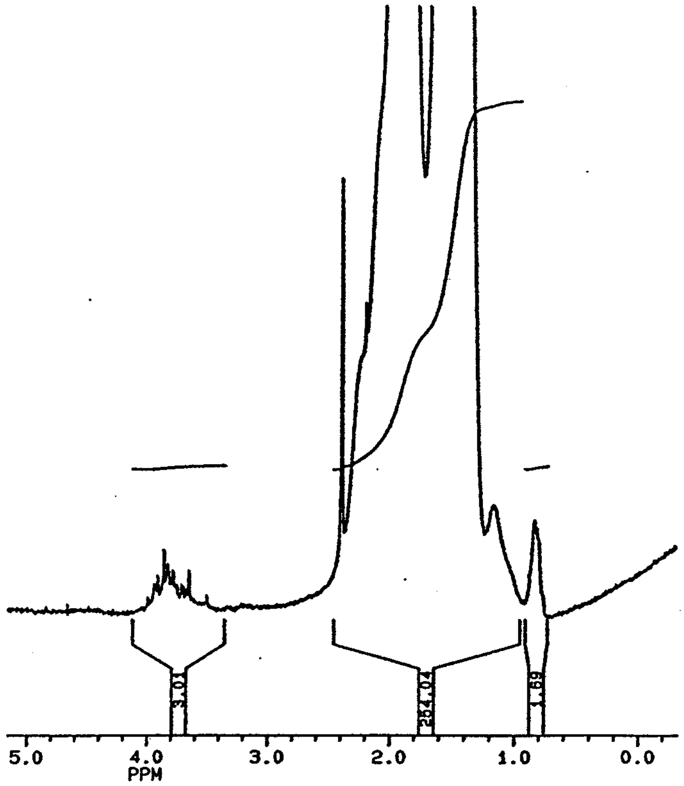

Figure 14. ^{1}H NMR of polystyrene reacted with dimethyl acetylenedicarboxylate

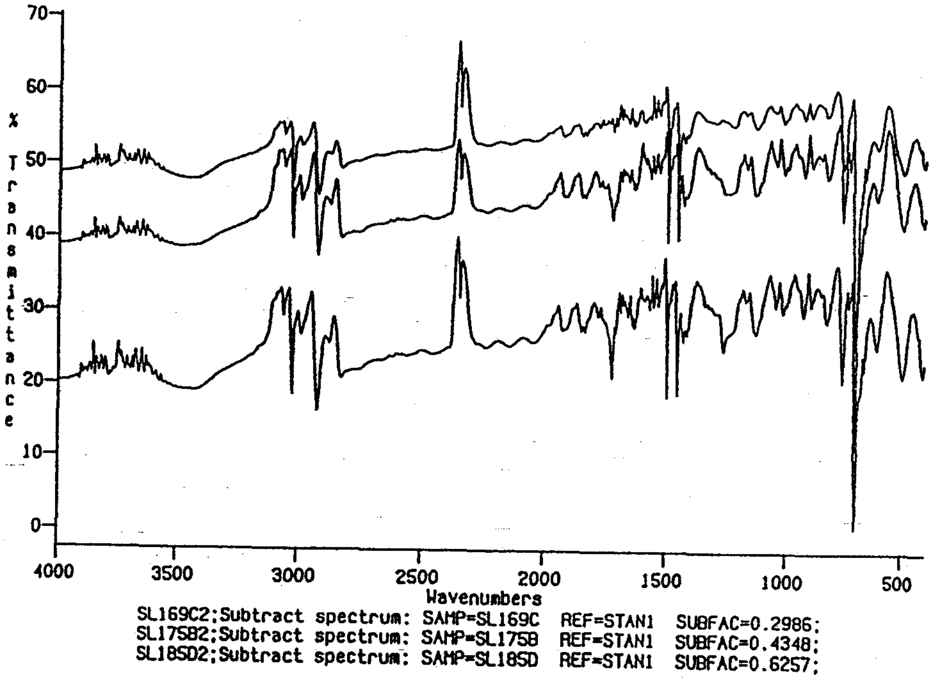

Figure 15. FTIR subtraction spectrum of polystyrene after Diels-Alder coupling with dimethyl acetylenedicarboxylate

Top curve : polystyrene sample before the coupling (sample No. sl169c)

Middle curve : polystyrene after the coupling (sample No. sl175b)

Bottom curve : polystyrene after catalyzed coupling (sample No. sl185d)

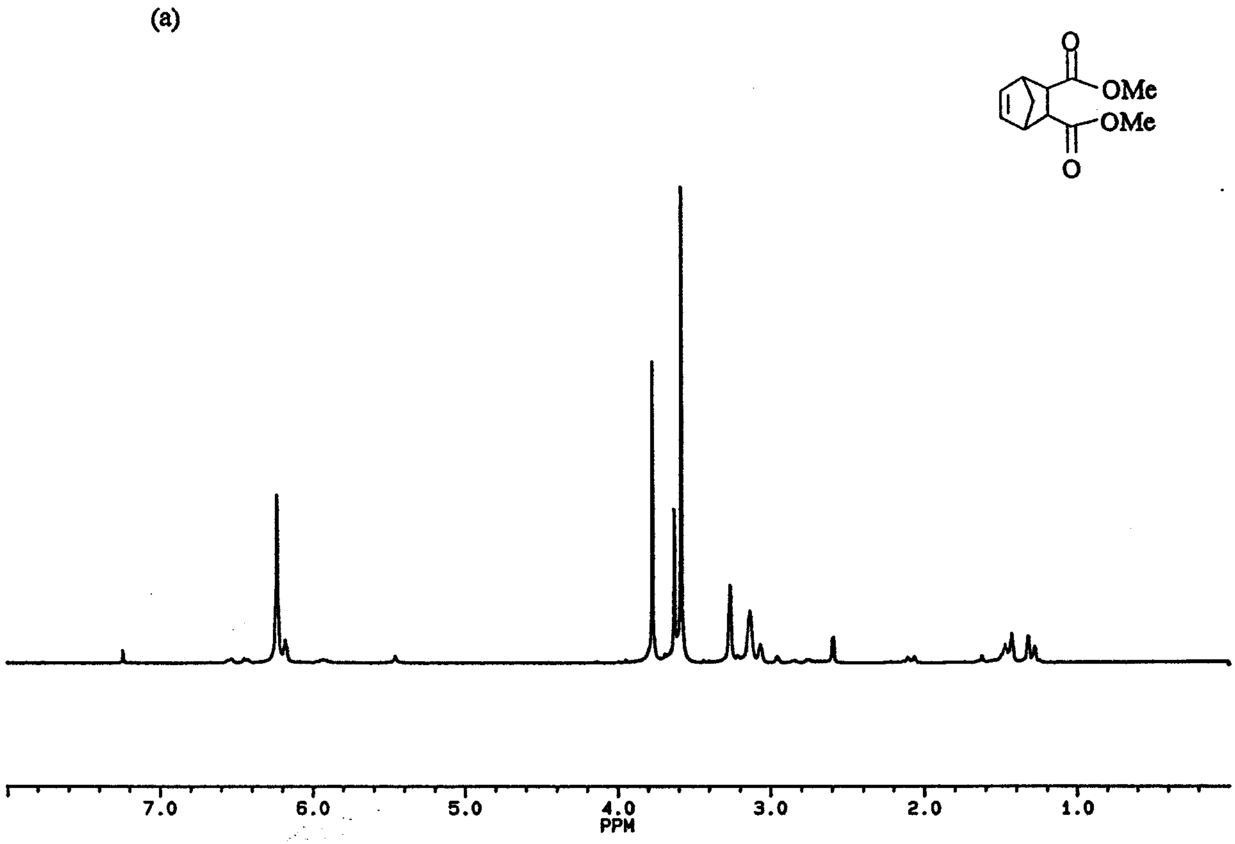

Figure 16. (a) ^{1}H NMR of the Diels-Alder coupling product of cyclopentadiene and dimethyl maleate

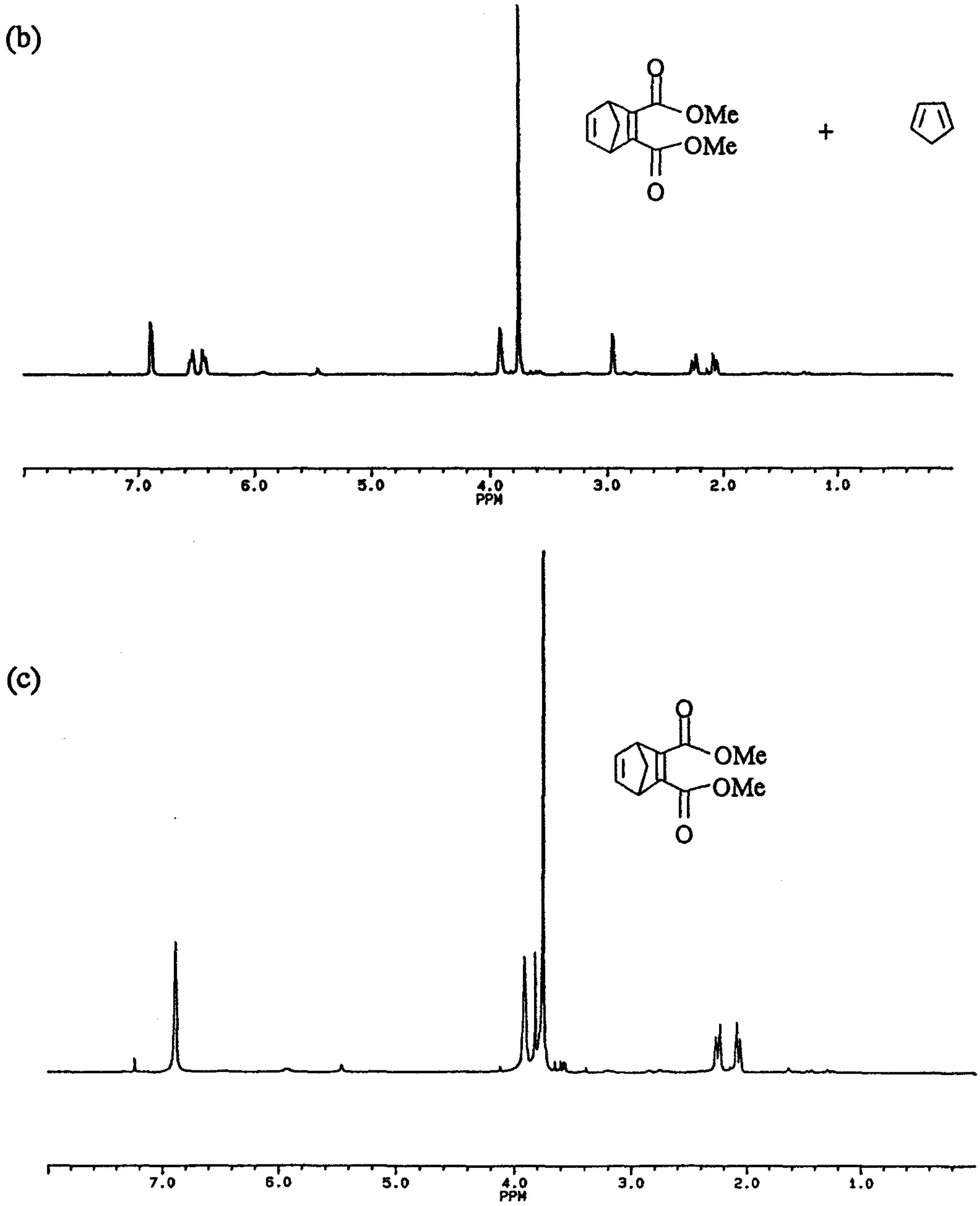

Figure 16. (b) ^{1}H NMR of the Diels-Alder coupling product of cyclopentadiene(2 mmol equiv.) and dimethyl acetylenedicarboxylate(1 mmol equiv.)

(c) ^{1}H NMR of the Diels-Alder coupling product of cyclopentadiene(1 mmol equiv.) and dimethyl acetylenedicarboxylte(1 mmol equiv.)

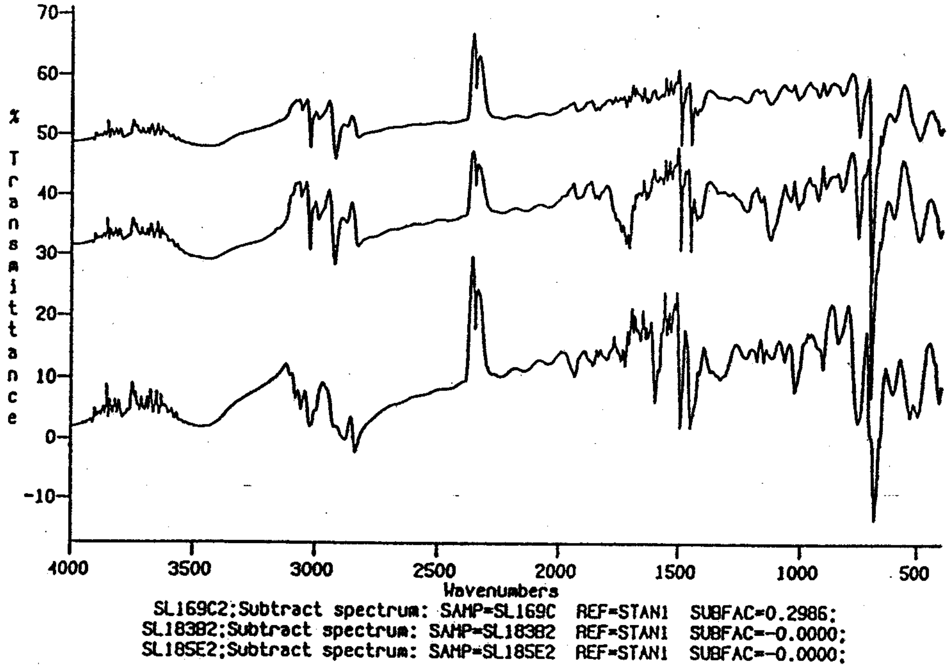

Figure 17. FTIR subtraction spectrum of polystyrene after ozonolysis

Top curve : polystyrene sample before ozonolysis (sample No. sl169c)

Middlecurve : polystyrene after ozonolysis in CH_2Cl_2 (sample No. sl183b)

Bottom curve : polystyrene after ozonolysis in THF (sample No. sl185e)

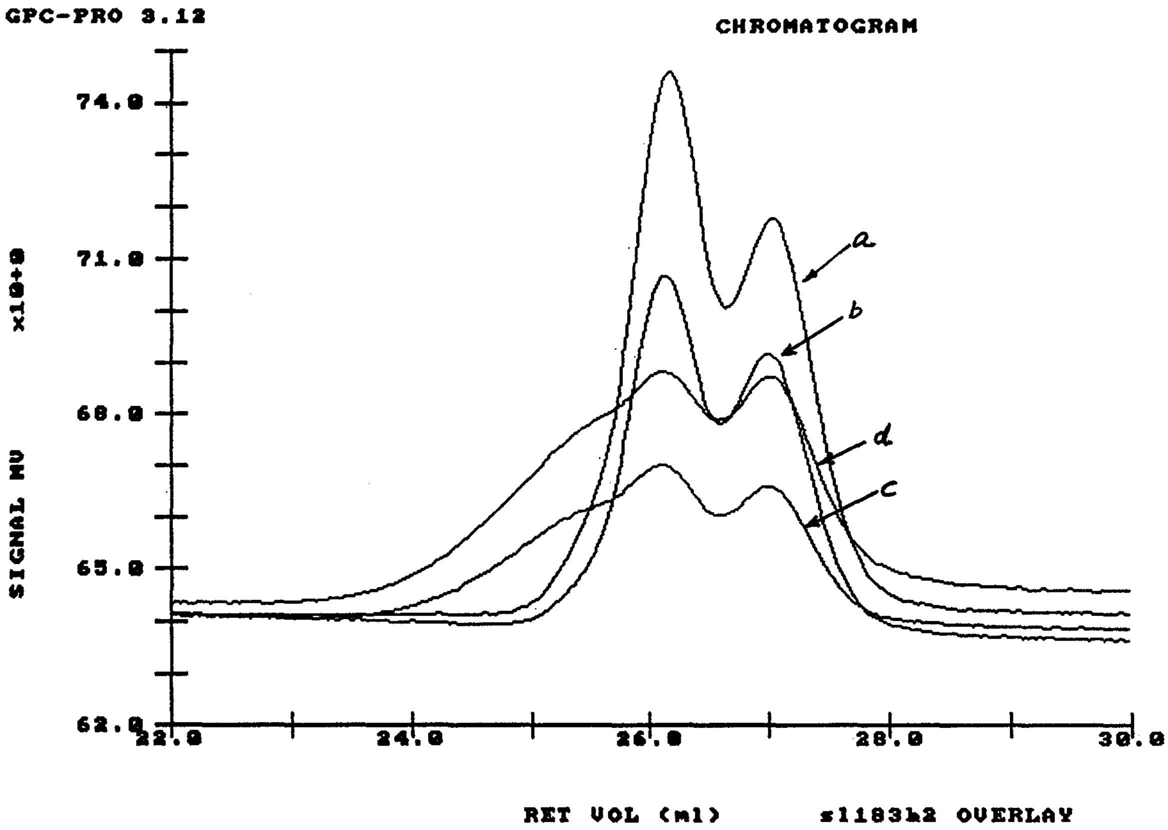

Figure 18. GPC chromatography of polystyrene after ozonolysis

Curve a : polystyrene sample before ozonolysis

Curve b : same sample after ozonolysis in THF solvent

Curve c : same polystyrene after ozonolysis in CH_2Cl_2 in 30 min.

Curve d : same reaction as curve (c) in 60 min.

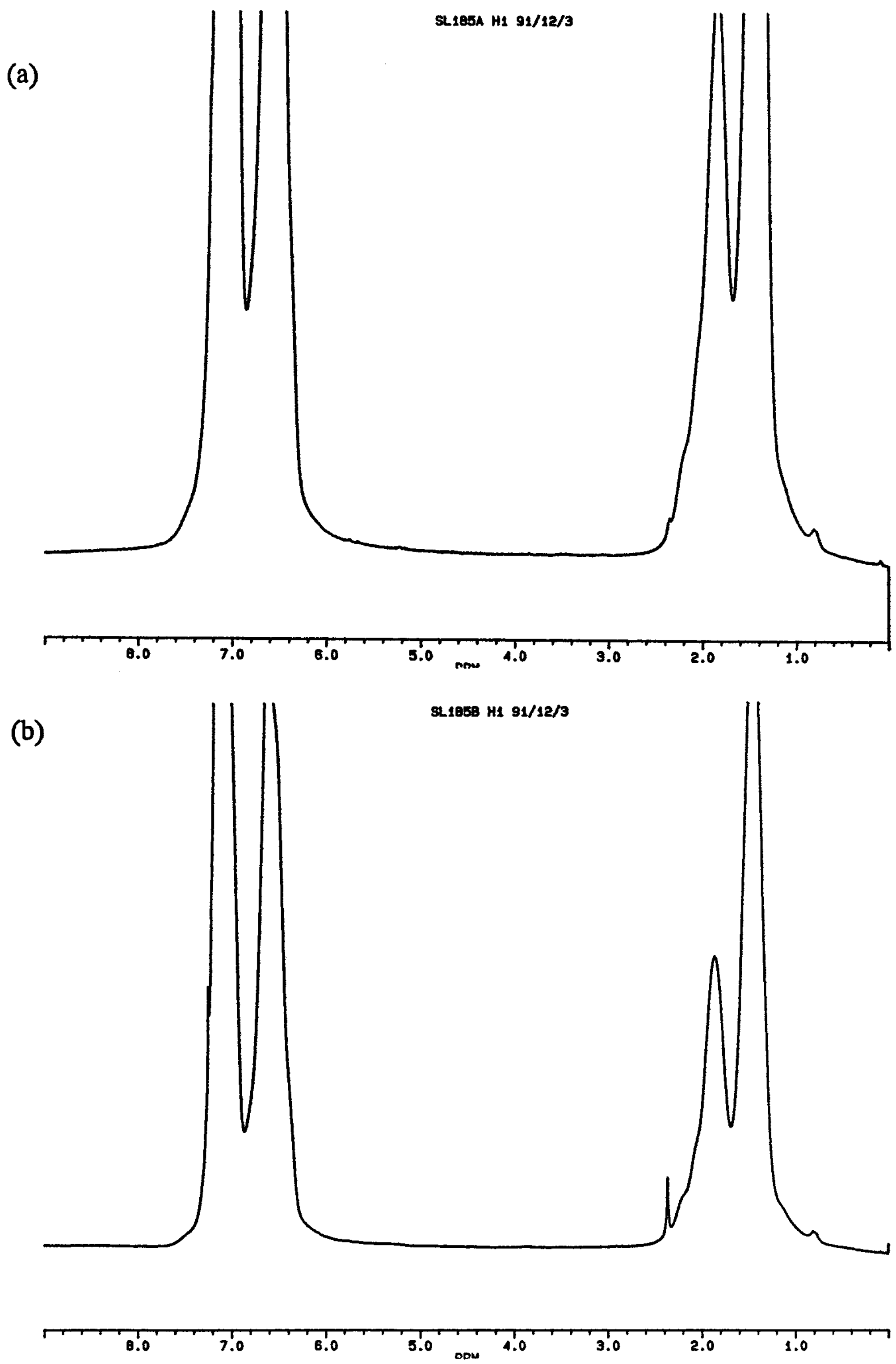

Figure19. ^{1}H NMR of polystyrene with methylamine group at chain center

(a) Methylamine group prepared from iodination of polystyrene

(b) Methylamine group prepared from bromination of polystyrene

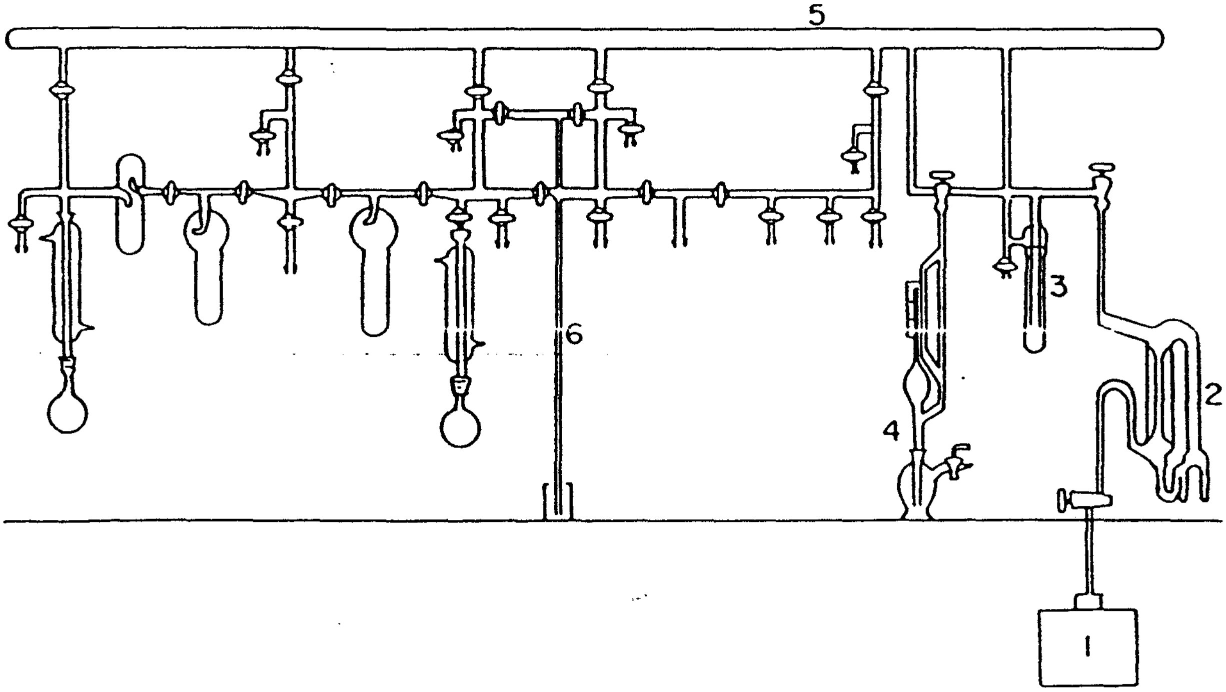

Figure 20. A typical vacuum system used in anionic polymerization

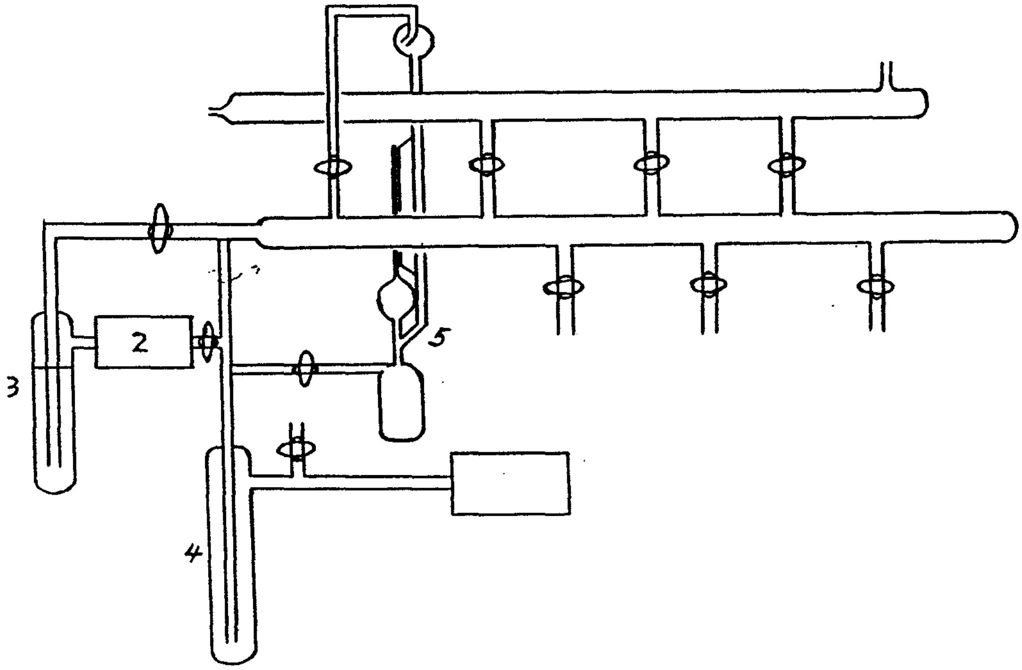

Figure21. High vacuum system used in this project

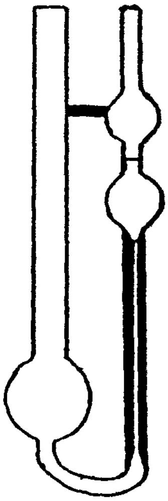

Figure 22. Cannon-Fenske Routine Viscometer

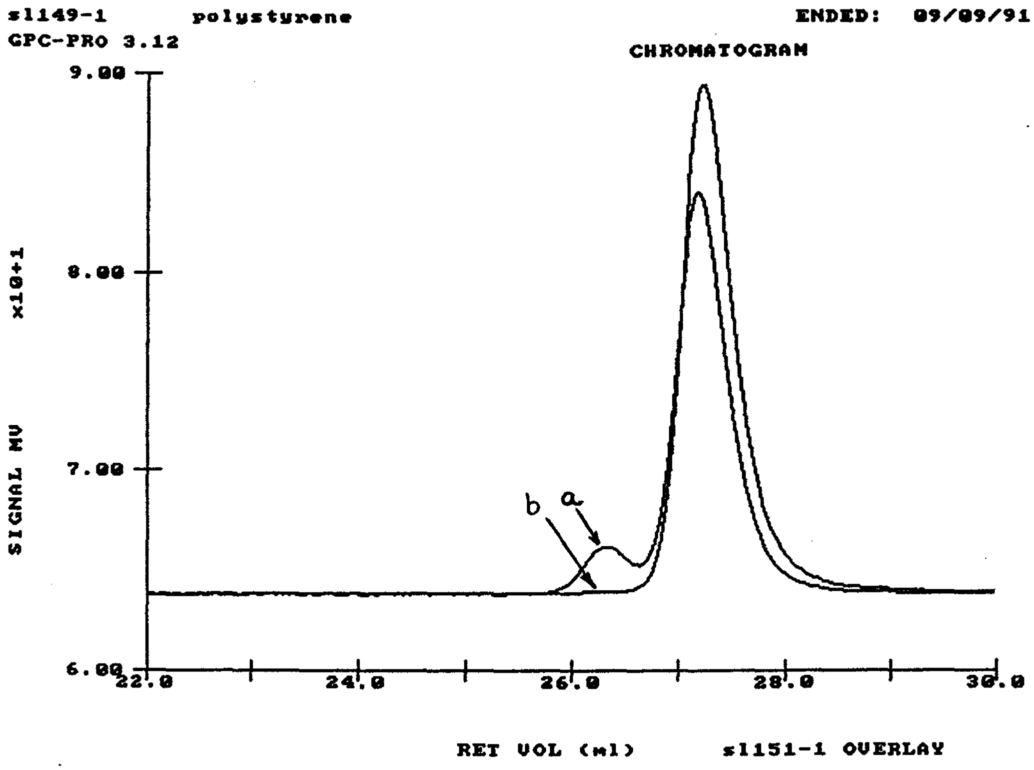

Figure 23. GPC chromatogram of polystyrene sample

curve a : living polystyrene injected into THF which is open to the air (sample No. sl149-1)

curve b : living polystyrene injected into THF in nitrogen (sample No. sl151-1)

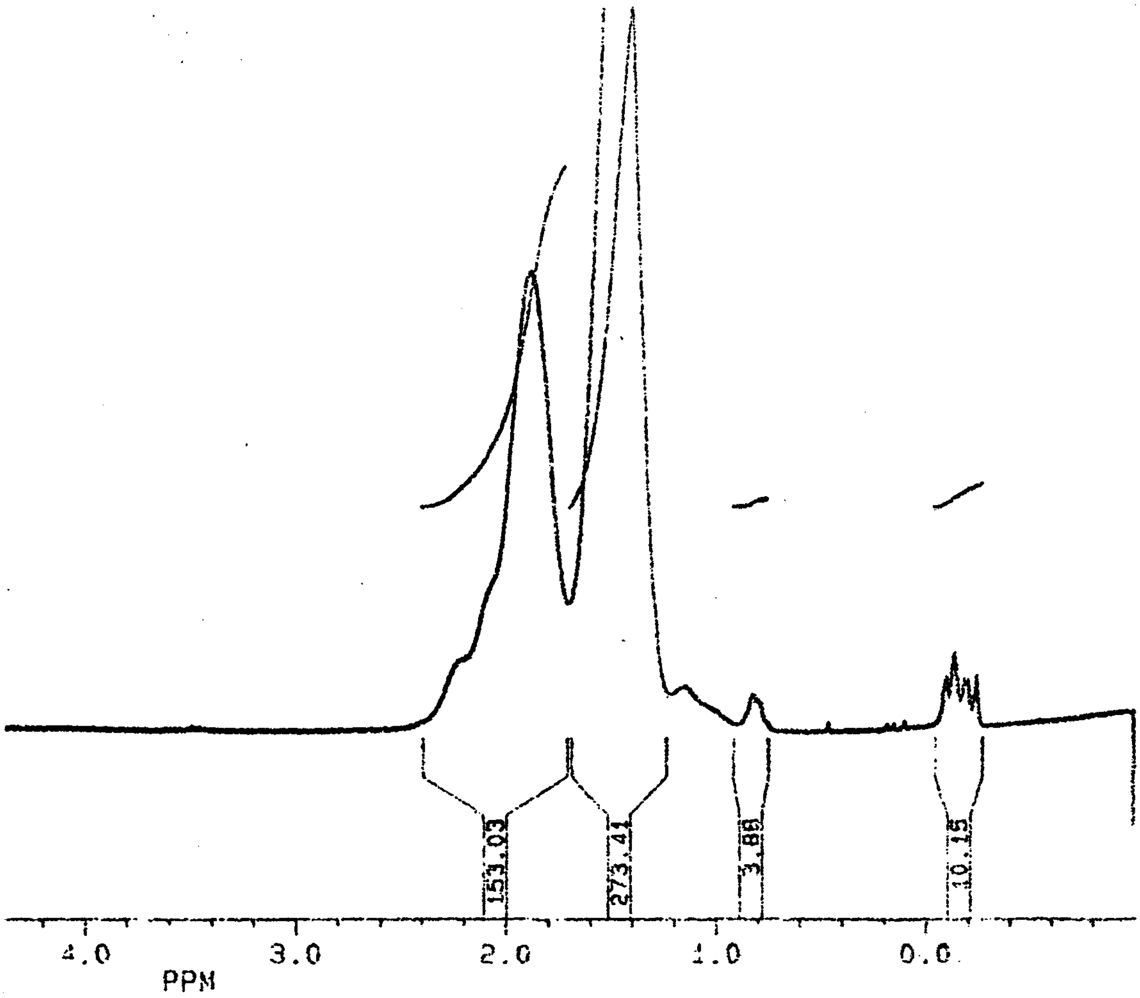

Figure 26. ^{1}H NMR of polystyrene terminated with trimethylchlorosilane