Radiation-Induced Pyrolysis of Poly(α-methylstyrene). Degradation by Cationic Chain Reactions

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ABSTRACT: It has been found that in the radiolysis of poly(α-methylstyrene) powder at high temperature under vacuum, monomer and a dimer, 1,1,3-trimethyl-3-phenylindane, are formed as volatile products and the molecular weight of the polymer apparently decreases, while in the conventional pyrolysis under the same conditions the only volatile product detected is monomer with a lower yield and the molecular weight of the polymer does not vary. The G values of the products and the scission of polymer chain were large enough to conclude that the degradation is due to chain reactions. It has been revealed by the effect of additives and comparison with the conventional pyrolysis that the radiation initiates the cationic chain reactions producing monomer and the dimer and causing the random scission of polymer chain as well as the radical chain reaction similar to that in the pyrolysis. The degradation appears to be facilitated above the glass transition temperature of the polymer.

Although degradation of polymers has widely been studied in many ways such as pyrolysis, oxidative degradation, photolysis, and radiolysis at ordinary temperature,[1] radiation-induced pyrolysis of polymers has not yet been examined. Most of the earlier investigations of radiation-induced pyrolysis have dealt with low molecular weight hydrocarbons, and it is known that the decomposition by the radical chain reactions similar to that in the conventional pyrolysis takes place below the temperature at which the pyrolysis occurs since the radiation facilitates the most energy-consuming process, that is, the formation of radicals by bond scissions.[2] Recently, cationic chain reactions have been observed to occur in the radiation-induced pyrolysis of alcohols[3] and n-butane.[4] The present study is concerned with the cationic chain reaction which is initiated by radiation and propagated at high temperature in a solid polymer system.

Pyrolysis of poly(α-methylstyrene) under vacuum has been studied by many workers, and it has been established that below about 400 °C the polymer decomposes almost completely into monomer by a radical chain reaction involving the "unzipping" process.[5] In a recent communication we reported that during the radiation-induced pyrolysis of poly(α-methylstyrene) powder under vacuum, a dimer, 1,1,3-trimethyl-3-phenylindane (TMPI), is formed as well as monomer, and a cationic chain mechanism has been proposed for its formation.[6] The present paper includes the results which demonstrate that the formation of monomer and the scission of polymer chain also occurs by the cationic chain reactions in this system. This seems to be the first example of the degradation of polymer by cationic chain reactions.

Experimental Section

Two kinds of poly(α-methylstyrene) were used for this investigation, one of which was prepared by the radiation-induced cationic polymerization in bulk under extensively dried conditions and had a number-average molecular weight ($\overline{M}_{n0}$) of 2.5×10^4. Another was prepared with a disodium α-methylstyrene tetramer as catalyst in tetrahydrofuran solution. The anionic polymer had an $\overline{M}_{n0}$ of 1.5×10^6 and a weight to number average molecular weight ratio of 1.2. The polymers were repeatedly dissolved in benzene and precipitated by methanol for purification and dried in a vacuum oven.

The polymer powder was evacuated at a pressure of $\sim 10^{-6}$mm Hg for more than 1 day in a Pyrex tube equipped with a cold finger and then sealed. The sample was heated in an electric furnace under the irradiation of ^{60}Co γ rays. The temperature was maintained constant to within 2 °C. A large portion of the volatile products were collected in the cold finger which was cooled with liquid nitrogen and protected by a lead block from the radiation. The yields of the products both trapped in the cold finger and remaining in the irradiated polymer were determined as follows. The products trapped in the cold finger were collected in a capillary, and the total yield of the products was determined by weighing the capillary before and after removing the products. The relative ratios of the products were determined by gas chromatography using an Apiezon L column. The yields of the products remaining in the irradiated polymer were also determined by gas chromatography. The irradiated polymer was dissolved in benzene containing a known amount of bibenzyl, an internal standard, and submitted to gas chromatography after separating the polymer by adding a small amount of methanol. The molecular weight distribution of the polymer was measured by a gel permeation chromatograph (Toyo Soda HLC 801), and the molecular weight was calculated from the chromatograph.

Polystyrene and poly(isobutyl vinyl ether) used as additives were prepared by the radiation-induced polymerizations. Another additive, linear polyethyleneimine, was obtained by the method in the literature.[7] The poly(α-methylstyrene) powder containing a small amount of the additive was prepared by the freeze-dry method from the dilute benzene solution. In the case of polyethyleneimine, which is insoluble in benzene, the benzene solution was heated above the melting point of the polymer, 58.5 °C, and stirred before freezing.

Results

Cationic Polymer ($\overline{M}_{n0} = 2.5 \times 10^4$). The polymer powder was irradiated at the dose rate of 9.2×10^5 rad/h at 200 °C under vacuum. The products trapped in the cold finger almost exclusively consisted of monomer and the dimer, TMPI. The dimer was also contained in the irradiated polymer, while the monomer almost completely passed over into the cold finger. The product yields and the ratio of the molecular weights before and after the degradation ($\overline{M}_{n0}/\overline{M}_{n_t}$) at a reaction time of 3 h are shown in Table I together with the results of the pyrolysis at 200 °C and the radiolysis at room temperature. The molecular weight of the polymer is reduced to about one-half its initial value in the radiolysis at 200 °C. On the other hand, when heated at 200 °C without irradiation, the only product detected is a smaller amount of monomer, and the molecular weight of the polymer does not vary. In the radiolysis at room temperature the product yields and the decrease in the molecular weight of the polymer are much smaller than those in the radiolysis at 200 °C. These results suggest that the radiation facilitates degradation at high temperature and that the mode of the degradation is distinct from that in the pyrolysis where the degradation by radical reaction occurs and polymer is known to decompose completely into monomer.[5]

The product yields and the $\overline{M}_{n0}/\overline{M}_{n_t}$ ratio increased linearly with irradiation time as shown in Figures 1 and 2. From the plots in Figure 1 the G values of monomer (G_m) and dimer (G_d) were determined to be 470 and 34, respectively. The G value of the scission of polymer chain (G_s) cannot be calculated from the decrease in the molecular weight since the decrease in the molecular weight is partially due to the product formation. However, if it is assumed that there is no consumption of polymer chain by the "unzipping" process of a

Table I
Radiolysis and Pyrolysis of the Cationic Poly(α-methylstyrene) ($\overline{M}_{n_0} = 2.5 \times 10^4$)[a]

	Temp, °C	Conversion, % Monomer	Conversion, % Dimer	$\overline{M}_{n_0}/\overline{M}_{n_t}$
Radiolysis	200	14	2.3	1.9
Radiolysis	23	0.27	0.05	1.1
Pyrolysis	200	2.1	[b]	1.0

[a] Reaction time is 3 h. The dose rate of the radiolysis is 9.2 × 10^5 rad/h. [b] Not detected.

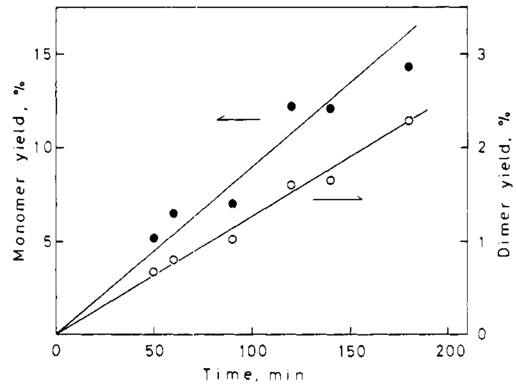


Figure 1. Conversions of monomer (●) and dimer (○) vs. irradiation time in the radiolysis of the cationic polymer ($\overline{M}_{n_0} = 2.5 \times 10^4$) at 200 °C and the dose rate of 9.2 × 10^5 rad/h.

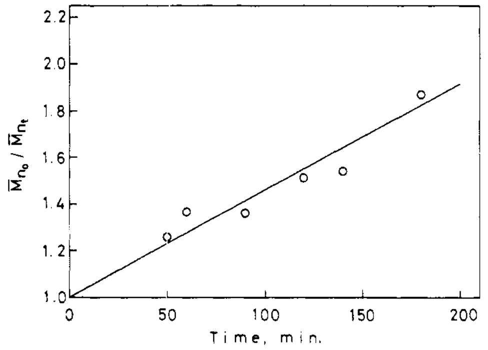


Figure 2. Ratio of the molecular weights before and after the degradation vs. irradiation time in the radiolysis of the cationic polymer ($\overline{M}_{n_0} = 2.5 \times 10^4$) at 200 °C and the dose rate of 9.2 × 10^5 rad/h.

kinetic chain length more than the molecular chain length, the G_s value, which corresponds to the minimum value, can be calculated from the following equations

$$N_s = \frac{6.02 \times 10^{23}}{M_{n0}}\left(\frac{M_{n0}}{M_{n_t}} \times \frac{W_t}{W_0} - 1\right)$$

$$G_s = 100N_s/r$$

where N_s is number of the scission of polymer chain (g^{-1}), W_0 and W_t are the weights of the polymer before and after the degradation (g), respectively, and r is radiation dose (eV/g). The minimum G_s value calculated is 8.4. Thus, the G_m, G_d, and minimum G_s values are large enough to conclude that the degradation is due to chain reactions.

Anionic Polymer ($\overline{M}_{n_0} = 1.5 \times 10^6$). In order to reveal the mechanism of the radiation-induced pyrolysis, the change of the molecular weight distribution of the polymer, the effect of additives, and the temperature dependence of the degradation were investigated using the anionic polymer having a narrow distribution of molecular weight. The rate of the degradation of this polymer was much larger than that in the case of the cationic polymer, and the experiments were carried out at the lower dose rate, 3.5 × 10^5 rad/h.

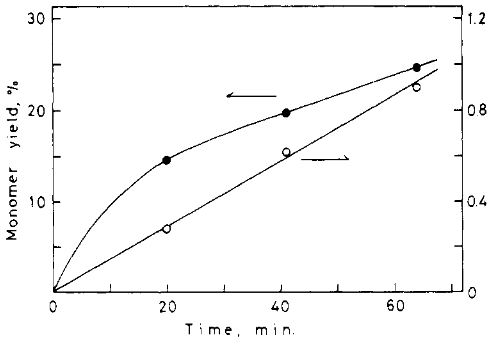


Figure 3. Conversions of monomer (●) and dimer (○) vs. irradiation time in the radiolysis of the anionic polymer ($\overline{M}_{n_0} = 1.5 \times 10^6$) at 195 °C and the dose rate of 3.5 × 10^5 rad/h.

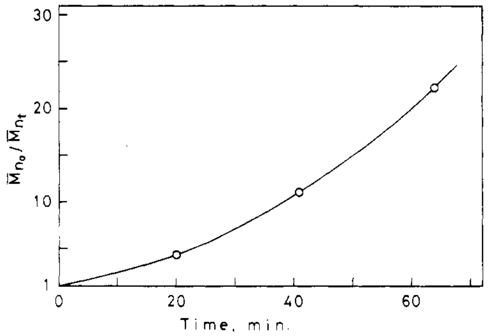


Figure 4. Ratio of the molecular weights before and after the degradation vs. irradiation time in the radiolysis of the anionic polymer ($\overline{M}_{n_0} = 1.5 \times 10^6$) at 195 °C and the dose rate of 3.5 × 10^5 rad/h.

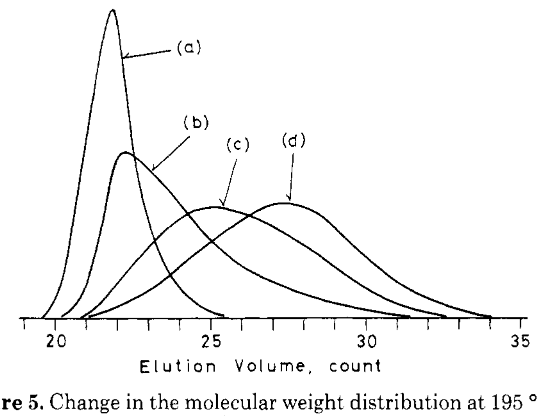


Figure 5. Change in the molecular weight distribution at 195 °C and the dose rate of 3.5 × 10^5 rad/h: (a) original polymer; irradiation times are (b) 20 min; (c) 41 min; and (d) 64 min.

The results of the radiolysis at 195 °C are shown in Figures 3, 4, and 5. The plots of the monomer yield and the $\overline{M}_{n_0}/\overline{M}_{n_t}$ ratio against irradiation time are not linear while that of the dimer yield is almost linear as shown in Figures 3 and 4. Figure 5 shows the change in the molecular weight distribution of the polymer. The molecular weight distribution becomes broader, and the peak position shifts to the larger elution volume with irradiation time, indicating that the random scission of polymer chain occurred.

Usually, in the radiolysis of hydrocarbons, the effect of the addition of cation scavengers such as amines, alcohols, and ethers, which have larger proton affinities than hydrocarbons, is investigated in order to obtain evidence for the cationic processes of product formation. In the present study, polymers were used as additives because any volatile additive is not

Table II
Radiolysis and Pyrolysis of the Anionic Poly(α-methylstyrene) ($\overline{M}_{n_0}$ = 1.5 × 10^6)[a]

	Temp, °C	Time, min	Additive (5 wt %)	Conversion, %		$\overline{M}_{n_0}/\overline{M}_{n_t}$
				Monomer	Dimer	
Radiolysis	195	64	none	25	0.90	22
Radiolysis	200	62	PS[b]	23	0.38	10
Radiolysis	203	62	PBVE[c]	18	0.05	2.7
Radiolysis	203	63	PEI[d]	12	[e]	1.6
Radiolysis	23	60	none	0.08	[e]	1.1
Pyrolysis	199	60	none	6.7	[e]	1.0

[a] The dose rate of the radiolysis is 3.5 × 10^5 rad/h. [b] Polystyrene. [c] Poly(isobutyl vinyl ether). [d] Polyethyleneimine. [e] Not detected.

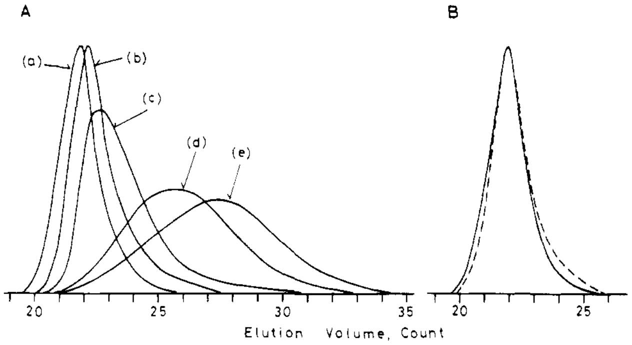


Figure 6. (A) Effect of additives on the change in the molecular weight distribution: (a) original polymer; additives, irradiation times, and temperatures are (b) polyethyleneimine, 63 min, 203 °C; (c) poly(isobutyl vinyl ether), 62 min, 203 °C; (d) polystyrene, 62 min, 200 °C; (e) none, 64 min, 195 °C, respectively. The concentration of the additives is 5 wt %. (B) Molecular weight distributions of the polymers after irradiated at room temperature for 60 min (dotted line) and heated at 199 °C for 60 min without irradiation (solid line).

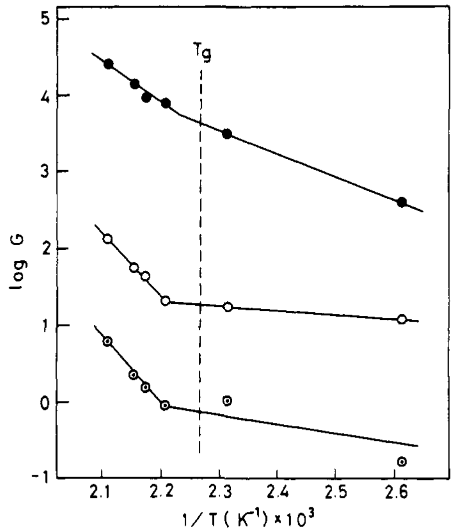


Figure 7. Arrenius plots of the G_m (●), G_s (○), and minimum G_s (⊙) values in the radiolysis of the anionic polymer at the dose rate of 3.5 × 10^5 rad/h. T_g shows the glass transition temperature of poly(α-methylstyrene).

suitable for the reaction at high temperature under vacuum. The effects of the additives, polystyrene, poly(isobutyl vinyl ether), and polyethyleneimine, are shown in Table II and Figure 6 together with the results of the pyrolysis and the radiolysis at room temperature. It appears that the product formation and the decrease in the molecular weight are suppressed by the addition of 5 wt % of the additives and that the efficiency of the suppression increases in the order polystyrene < poly(isobutyl vinyl ether) < polyethyleneimine. Since the proton affinity of the additive is considered to increase in the same order,[8] the result reveals that cationic reactions contribute to the degradation. By the addition of polystyrene, which is not regarded as a cation scavenger in the present system, the degradation is suppressed to some extent. This effect may be attributed to the chain transfer from poly(α-methylstyrene) to polystyrene.[9]

The result of the pyrolysis demonstrates that the degradation by radical reactions does not result in the formation of the dimer and the decrease in the molecular weight of polymer. In the radiolysis at high temperature the formation of the dimer and the decrease in the molecular weight of the polymer are almost completely suppressed by the addition of polyethyleneimine which is the most effective cation scavenger used. On the other hand, monomer is formed with a certain yield in the presence of polyethyleneimine, and the yield is much larger than that in the pyrolysis under the nearly same conditions. The effect of the addition of polyethyleneimine on the pyrolysis was examined at 200 °C and a reaction time of 1 h. Addition of 5% polyethyleneimine reduced the monomer yield only by a factor of 1.3. The efficiency of the suppression of the monomer formation is apparently smaller than that in the radiolysis at high temperature. Such a result suggests that the monomer formation in the radiolysis at high temperature is partially due to cationic reactions. Thus, although polyethyleneimine acts as a radical scavenger, the effect is considered to be apparently smaller than that on cationic reactions. On the basis of these results it seems reasonable to conclude that the formation of the dimer and the decrease in the molecular weight of the polymer are exclusively due to cationic reactions, while the thermally and radiolytically initiated radical reactions contribute to the formation of monomer as well as cationic reactions. Figure 6 shows that the change in the molecular weight distribution is vanishingly small in the presence of polyethyleneimine as well as that in the pyrolysis and the radiolysis at room temperature.

The G_m, G_d, and minimum G_s values were determined in the temperature range from 200 to 110 °C. At higher temperatures near 200 °C the plots of the monomer yield and the $\overline{M}_{n_0}/\overline{M}_{n_t}$ ratio against irradiation time apparently deviated from linear relationship, and in such cases the G values were determined from the initial slopes of the plots. The temperature dependence of the G values is shown in Figure 7. The Arrenius plots of the G values appear to be broken at the same temperature, about 180 °C, which is close to the glass transition temperature of this polymer, 168 °C,[10] and it is suggested that the degradation is facilitated above the glass transition temperature. The G_m, G_d, and minimum G_s values at 200 °C are 25 000, 110, and 5.9, respectively.

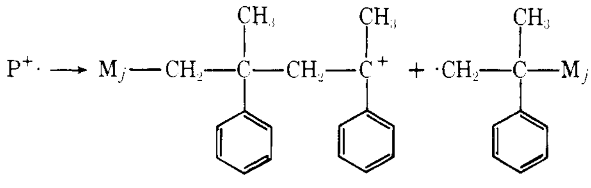
Discussion

The previous studies on the conventional pyrolysis of poly(α-methylstyrene) under vacuum have been carried out with molten thin films, and the lowest temperature studied is 226 °C.[5] The present experiments were carried out with solid powders at the lower temperatures near 200 °C. The monomer yield was much larger in the higher molecular weight polymer (anionic) than that in the lower molecular weight polymer (cationic), and the molecular weight of the polymer did not vary in both cases. These results suggest that the kinetic chain length of the radical "unzipping" process is larger than the molecular chain length of the polymers. It has been shown in the previous studies using anionic polymers that the molecular weight of the polymer decreases during the pyrolysis.[5c,d] A probable explanation for the difference in the results between this and previous studies is that in solid powders at lower temperature the intermolecular chain transfer and the bimolecular termination are suppressed and a polymer chain completely decomposes into monomer by the "unzipping" process once a bond scission occurs.

In the radiolysis at high temperature the radiation-induced pyrolysis occurs as well as the conventional pyrolysis. It was shown that in the radiation-induced pyrolysis the formations of monomer and TMPI and the scission of polymer chain occur by cationic chain mechanisms, and monomer is also formed by the radical chain reaction similar to that in the pyrolysis. The dimer is known to be formed in the acid-catalyzed dimerization of α-methylstyrene together with linear dimers.[11] It is also known that in the cationic polymerization of α-methylstyrene by catalyst a 1,3-dimethyl-3-phenylindanyl end group is formed by the electrophilic substitution of the penultimate benzene ring by the propagating cation.[12] These facts suggest that the dimer is formed by the reaction of the carbonium ion produced by irradiation.

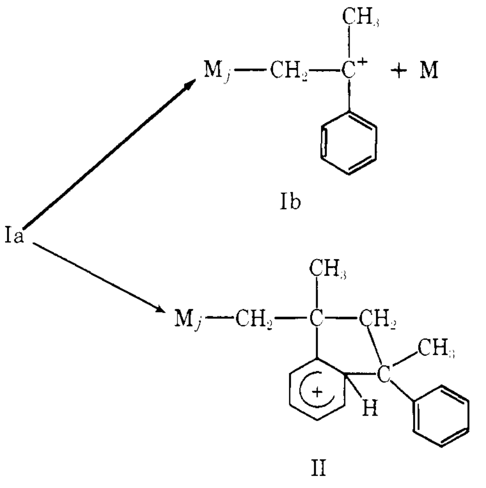
The mechanism of the cationic processes in the radiation-induced pyrolysis can be considered as in reactions 1–5, where P and M denote a polymer chain and a monomer unit, respectively. The stable carbonium ion (Ia) is produced from the polymer cation, $P^{+\cdot}$, and gives monomer by the cationic "unzipping" process (reaction 3) or the carbonium ion (II) by the chain end cyclization analogously to the propagating cation in the polymerization.[12] The dimer is formed from II by the reaction 5, which is regarded as an intramolecular protolysis of the C–C bond by the proton derived from the aromatic ring. The protolysis of a C–C bond has recently been reported in the studies using super acids.[13] The result of the present study seems to suggest that at high temperature the protolysis of the weak C–C bond generating the stable tertiary carbonium ion occurs by the proton from the carbonium ion. Thus, it is reasonable to assume that the random scission of polymer chain is also caused by the protolysis, that is, the chain transfer of the scission of polymer chain is the intra- or intermolecular proton transfer followed by the protolysis of polymer chain

$$P \rightsquigarrow P^{+\cdot} + e \qquad (1)$$



(2)

Ia

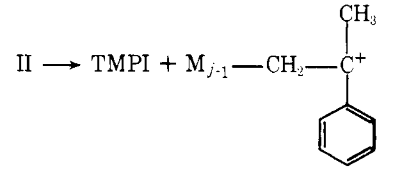


(3)

Ib

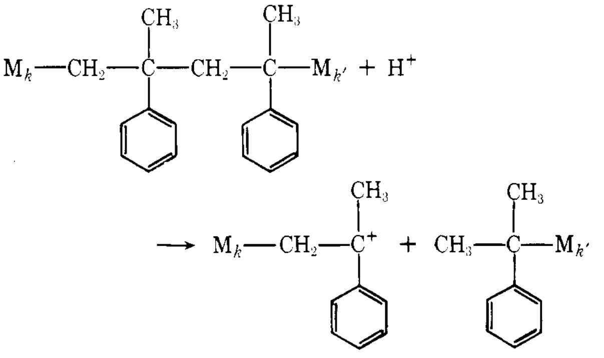
(4)

II



(5)

Ic



(6)

Id

where the proton is derived from the carbonium ion I or II. The extensive decrease in the molecular weight in the radiation-induced pyrolysis demonstrates that the cationic chain transfer certainly occurs in contrast to the radical chain transfer in the pyrolysis. In the presence of the additive having a larger proton affinity than the hydrocarbon, the proton transfer from the carbonium ion I or II to the additive occurs, and the chain reaction is terminated. In the radiolysis at high temperature radicals are produced by thermal and radiolytic homolytic fissions and by heterolytic fissions such as reaction 2. These radicals initiate the degradation which is similar to that in the pyrolysis.

The results of the present study demonstrate that the cationic "unzipping" process giving monomer and the dimer occurs during the radiation-induced pyrolysis as well as the radical "unzipping" process whose kinetic chain length is larger than the molecular chain length of the polymers used. As is shown above, the G_d value at 200 °C is apparently larger in the higher molecular weight polymer (anionic) than that in the lower molecular weight polymer (cationic) as well as the G_m value. Such a result may suggest that the polymer cation (I) having molecular chain length less than the kinetic chain length of the cationic "unzipping" process is appreciably produced by the random scission in the case of lower molecular weight polymer and that its complete decomposition results in the termination of the reaction. However, the possibility that the difference in the physical properties between these polymer powders is responsible for the result cannot be ruled out at the present time.

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Hammett Relations in Anionic Polymerization. Reaction of Polystyrylalkali Salts with Disubstituted 1,1-Diphenylethylenes

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ABSTRACT: In order to obtain a better understanding of the role of the cation and of the carbanionic part of the active center in the growth step of anionic polymerizations in nonpolar media, the Hammett relation was examined for the reaction of various disubstituted 1,1-diphenylethylenes with the Li^+, K^+, and Cs^+ salts of living polystyrene in benzene at 24 °C, diphenylethylenes being chosen as monomers because they do not further polymerize after one addition step and allow a simple spectrophotometric determination of the rates. The Hammett plots all yielded positive ρ values, increasing from ca. +1.8 for the Li^+ salt to +2.2 for the K^+ salt and +2.4 for the Cs^+ salt. These values, which all pertain to the reaction of ion pairs containing different cations, are to be compared with the ρ value of +2.8 to +3.5 obtained for the same type of reaction with the K^+ salt of living polystyrene in THF, where ρ may be assumed to be largely determined by the reaction of free carbanions. The results combined with some known data from the literature suggest that in the absence of stronger coordinating molecules, such as ethereal solvents, complexation of the monomer with the positive counterion or participation of this ion in polarizing the double bond of the monomer constitutes a characteristic feature of the propagation reaction of anionic polymerization in the presence of alkali salts, at least with lithium as a counterion. In order to check a possible influence of the π electrons of benzene, the addition of the different disubstituted diphenylethylenes to the Li^+ salt of living polystyrene was also studied in cyclohexane, allowing a direct comparison with the results obtained for this salt in benzene.

During the last decade, much attention has been paid in mechanistic studies of anionic polymerizations to solvent effects or to complexation of the active species with different donor agents. However, in spite of the vast amount of results, the detailed mechanism of the main step of the polymerization process (the propagation reaction) is still not clear, particularly for polymerizations of vinyl monomers in nonpolar solvents with alkali metals as counterions.

The question arises as to whether the C=C bond of the monomer could participate in the coordination with the positive counterion, prior to its addition to the polymeric chain end, if other coordinating agents, like ethers, are absent. Although no direct proof was provided for complex formation with the monomer during anionic chain propagation, some spectroscopic evidence was found for monomer–counterion type complexes in compounds such as 3-butenyl-[1] or 5-methyl-2-heptenyllithium.[2] Two types of anionic polymerizations are contemplated:[3–6] the direct one-step propagation and the two-step reaction in which the monomer is first associated with a cation yielding an intermediate complex, whereafter the spontaneous rearrangement of the latter produces the original living polymer but by one unit longer.

The latter mechanism was discussed by Medvedev[5] and seems to be plausible in anionic polymerizations proceeding in nonpolar media with lithium as counterion. Formation of such a complex may account for the stereospecificity of diene polymerization induced by organolithium compounds in nonpolar media. In fact, substitution of Li^+ by Na^+ and K^+ decreases the 1,4-cis content.[5,7]

Two observations support the hypothesis that the coordination of monomer with cation is operative in chain growth. The second order with respect to the monomer concentration, as observed in studies of polymerization of isoprene,[8] was accounted for by assuming chain growth involving an activated monomer formed by an association of isoprene with a monomeric growing chain end.

Similarly, in the reaction of butyllithium (BuLi) with a large excess of styrene in benzene, π-complex formation between the Li^+ cation and styrene, which would break up the hexameric aggregates of BuLi into trimers, was suggested to explain the observed one-third order with respect to the BuLi concentration, instead of the usual one-sixth order in this nonpolar solvent.[9] The slowing down of the reaction rate by carrying out the polymerization in the presence of durene, being a better complexing agent than the monomer, seemed to support this assumption.[10]

The problem of monomer complexation resulting in a two-stage propagation reaction leads to the interesting question which stage is the rate-determining step in such systems? Further information about this may be obtained from Hammett relation studies. Indeed work by Natta et al.[11] indicated a negative ρ value ($\rho = -0.95$) for the anionic co-