Equilibrium Anionic Polymerization of p-lsopropyl-α-methylstyrene in Tetrahydrofuran

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ABSTRACT

The equilibrium anionic polymerization of p-isopropyl-α-methylstyrene in tetrahydrofuran with potassium and sodium-naphthalene complex as initiators has been investigated in the temperature range of -20 to +20°C by use of high-vacuum techniques. The comparison of these results with those obtained previously for the equilibrium polymerization of α-methylstyrene revealed that, because of the p-substituted bulkier isopropyl group in the monomer, the values of $\Delta G_{\ell c}$, the free-energy change upon the polymerization of 1 mole of liquid monomer to 1 base-mole of liquid amorphous polymer of infinite chain length, are slightly higher in the present studies. The values of $\Delta H_{\ell c}$ and $\Delta S_{\ell c}$ computed from the plots of $\Delta G_{\ell c}/RT$ versus $1/T$ yielded values which are lower than that for the α-methylstyrene-THF system. The effect of p-substitution is also observed in the higher values of the monomer equilibrium concentration $[M]_e$ and lower values of β [$\beta = \chi_{ms} - \chi_{sp}(V_m/V_s)$],

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where χ_{ms} and χ_{sp} are monomer-solvent and solvent-polymer interaction parameters, respectively, and V_m/V_s is molar volume ratio of monomer to solvent. The values of χ_{ms} for the p-isopropyl-α-methylstyrene-THF system increase regularly with increasing temperature, whereas in α-methylstyrene-THF system the increase in χ_{ms} was not that marked

INTRODUCTION

In recent years, the equilibrium polymerizations of styrene [1-4], α-methylstyrene [5-10], and a number of phenyl-substituted styrenes [2, 8] have been investigated. It was noted that the substitutions in the benzene ring of styrene did not affect the thermodynamic parameters, enthalpy of polymerization ΔH_{SS} and entropy of polymerization ΔS_{SS} [8]. However the substitution of an α-methyl in the vinyl part of styrene increased the value of $\Delta H_{\ell c}$ from about -17.4 [3] to -10.9 kcal/mole [9]. The values of $\Delta S_{\ell c}$, on the other hand, decreased from -24.8 [3] to -35.4 cal/deg-mole [9]. In order to explore the effect of additional substitution in α-methylstyrene on the values of equilibrium monomer concentration [M_e], the free energy change $\Delta G_{\ell c}$, enthalpy of polymerization $\Delta H_{\ell c}$, and the entropy of polymerization $\Delta S_{\ell c}$, anionic equilibrium polymerization of p-isopropyl-α-methylstyrene was carried out in tetrahydrofuran (THF) at six different temperatures using sodium-naphthalene complex and potassium mirror as initiators. The values of $\Delta G_{\ell c}$, $\Delta H_{\ell c}$, and $\Delta S_{\ell c}$ have been computed in the same way as that for the α-methyl-styrene-THF system [9]. The principal results of these studies form the subject of the present communication.

EXPERIMENTAL

Materials

p-Isopropyl-α-methylstyrene (Aldrich Chemical Company, density at 22.2°C = 0.885 g/dl), was kept over calcium hydride and degassed on the vacuum line for two weeks. It was distilled under vacuum, the head and tail fractions being discarded. Vapor-phase chromatography of the middle fraction showed that there were no impurities

present. It was further confirmed by infrared and NMR spectroscopy. Prior to use, the monomer was further purified by distilling it on a mirror of sodium metal.

Tetrahydrofuran (THF) (Fisher Scientific Co.) was purified in the same manner.

Polymerizations

Polymerizations with potassium alone were carried out in a fashion similar to that for α-methylstyrene described elsewhere [10, 11] in detail. These were carried out in ampoules which were provided with side tubes for making mirrors of pure metal and distillation of THF followed that of the monomer. With sodium-naphthalene complex as initiator, polymerizations were carried out in Pyrex ampoules which had side tubes carrying complex of sodium-naphthalene in THF and were connected with the ampoule through a breakseal arrangement.

After having distilled the required amounts of monomer and solvent the glass ampoules were sealed off the line and the reaction was initiated. Once the desired concentration of living ends was incorporated in the solution, the side tube was removed and the main ampoule was brought to the temperature of polymerization. Progress towards equilibrium was followed through the variation of the meniscus height in the ampoule. After the equilibrium had been reached (24 hr at -20°C to 3 days at 20°C), the ampoule was opened to air at the equilibrium temperature and the reaction was terminated by the addition of methanol. After the red color had disappeared, the solution was quantitatively removed and the polymer precipitated in methanol. The precipitated polymer was filtered through a weighed sintered glass filter, thoroughly washed with methanol, and dried to a constant weight in a vacuum oven at 60°C. The filtrate and the washings were collected in a measuring flask and preserved for the analysis of the unreacted p-isopropyl-α-methylstyrene.

Monomer Analysis

Determination of unreacted monomer was carried out through gas chromatographic analysis with cumene as internal standard. Analyses were performed with a Perkin-Elmer Chromatograph at 190°C on a UCON oil column LB-550-X with the use of thermal conductivity detector and helium as carrier.

Molecular Weights

The flow time of polymer solutions with concentrations of about 0.2% were measured at 25°C in toluene by using a modified Ubbelohde

viscometer [12]. The intrinsic viscosity [η] was obtained by the one-point method [13]. For the present system, results obtained by the one-point method were in good agreement with those obtained through the extrapolation of η_{sp}/c versus c. Molecular weights were computed from the relationship [14] (1):

$$[\eta] = 4.5 \times 10^{-4}\,\overline{M}^{0.55} \tag{1}$$

Concentration of "Living Ends" $[LE]_0$

Assuming two "living ends" per chain, $[LE]_0$ may be obtained from the relationship

$$[LE]_0 = 2\,W/\overline{M}_n\,V_e \tag{2}$$

where W is the weight of the polymer (in grams) present at equilibrium in the volume V_e (in liters), and $\overline{M}_n$ is the number-average molecular weight. For the sake of convenience one may also use $\overline{M}$ (calculated from the viscosity data) in place of $\overline{M}_n$ if it can be shown that the polymers produced have narrow molecular weight distributions, is considered as a characteristic trait of living anionic polymerizations. This, however, is not completely true, as has been shown in the case of poly-α-methylstyrene prepared in THF with potassium as initiator, where these distributions were either broad or even multimodal in character [15]. In such cases, the living end concentration value calculated from Eq. (2) is not $[LE]_0$ but in reality

$[LE]_{effective}$, because the contribution of low molecular weight oligomers (where a major portion of $[LE]_0$ is tied up) towards viscosity is less important as compared to that due to the high molecular weight polymer. Thus, sometimes it is more rewarding to know $[LE]_{effective}$, which controls a major part of polymerization, than $[LE]_0$ and in that context the living end concentration of the chain ends by viscosity yields a better index for comparison than $[LE]_0$. In the present polymers, the gel-permeation chromatographic studies on the distribution of molecular weight have shown [11] these to be broad in nature. In the present system, therefore, the $[LE]_{effective}$ has been calculated by using Eq. (2) and these are of the order of 10^{-2} to 10^{-3} mole/liter.

RESULTS AND DISCUSSION

Equilibrium monomer concentration $[M]_e$ and equilibrium polymer concentration $[P]_e$ for the anionic polymerization of p-isopropyl-α-methylstyrene in THF at -20, -5, 0, 5, 15, and 20°C are shown in Table 1 together with molecular weights $\overline{M}$ and living end concentration $[LE]_{effective}$. Plots of $[M]_e$ versus $[P]_e$ based on the data in Table 1 are shown in Fig. 1. It may be mentioned here that at low temperature, e.g., -20°C it is impossible to do experiments with $[M]_0$ higher than 1.0 or around that because of the formation of gels.

As has been mentioned in an earlier publication [11], the polymers prepared with anionic initiators as well are branched in character, and once the degree of branching exceeds a certain limit, microgels and complete gels are formed. However, before this stage of microgels is reached, the variation of $[M]_e$ with $[P]_e$ is linear, as was the case for the α-methylstyrene-THF as well as the α-methylstyrene-p-dioxane [10] system. This variation may be expressed by Eq. (3), where A and B are constants whose values vary with temperature.

$$[M]_e = A + B[P]_e \tag{3}$$

In order to relate the experimental results to the thermodynamic properties of the polymer system, Eq. (3) has to be written in terms of monomer volume fraction ϕ_m and the polymer volume fraction ϕ_p. Thus

$$\phi_m = AV_m + B(V_m/V_p)\phi_p = \phi_m{}^0 + b\phi_p \tag{4}$$

where V_m is the monomer molar volume and V_p the apparent volume of one base-mole of polymer in solution. The values of V_m and V_p used in the present system were found experimentally by studying the changes in volume for pure monomer as well as a 24% solution of the polymer in the monomer. Values of A, B, V_m, V_p, $\phi_m{}^0$, and ϕ_p are shown in Table 2.

The variation of ϕ_m with ϕ_p may be expressed [16] by

$$\phi_m = \frac{-(\Delta G_{\ell c}/RT) + \ln a + \beta}{\beta + \chi_{mp} - (1/a)} + \frac{\chi_{mp} - \beta}{\beta + \chi_{mp} - (1/a)}\phi_p \tag{5}$$

TABLE 1. Equilibrium Values of Monomer and Polymer Concentrations, Molecular Weights, and Living End Concentrations at Various Temperatures

Solvent	Temperature (°C)	$[M]_e$ (mole/ liter)	$[P]_e$ (base-mole/ liter)	$\overline{M} \times 10^{-4}$ (g/mole)	$[LE] \times 10^3$ (mole/liter)
THF	-20	0.38	0.36	16.3	0.7
		0.36	0.53	210.0	0.1
		0.37	0.54	52.5	0.3
		0.37	0.61	55.6	0.3
		0.36	0.62	38.0	0.5
		0.36	0.71	177.8	0.1
		0.33	0.80	251.2	0.1
THF	-5	0.90	0.23	4.0	1.8
		0.85	0.34	12.9	0.8
		0.86	0.35	5.0	2.2
		0.82	0.52	304.8	0.05
		0.80	0.54	10.0	1.7
		0.78	0.71	14.8	1.5
		0.75	0.87	208.9	0.1
THF	0	0.92	0.51	0.6	27.9
		0.70	0.71	0.7	33.0
		1.00	0.82	3.0	8.8
		0.94	1.13	8.0	9.8
		0.84	1.45	13.1	3.5
		0.67	2.19	15.8	4.4
THF	5	1.20	0.34	0.6	11.8
		1.16	0.43	0.8	17.1
		1.03	0.94	0.9	32.9
		1.08	1.14	2.0	18.1
		0.98	1.50	2.6	18.2
		0.95	1.61	5.8	8.7

TABLE 1. (cont.)

Solvent	Temperature ($^\circ$C)	$[M]_e$ (mole/ liter)	$[P]_e$ (base-mole/ liter)	$\overline{M} \times 10^{-4}$ (g/mole)	$[LE] \times 10^3$ (mole/liter)
THF	5	0.84	2.07	27.9	2.3
		0.80	2.24	7.9	4.5
		0.75	2.40	59.2	1.3
THF	15	2.06	0.15	0.6	7.7
		1.94	0.44	0.8	17.8
		1.90	0.70	11.0	2.0
		1.83	1.01	23.7	1.3
		1.75	1.16	56.0	0.6
		1.62	1.69	10.9	4.9
		1.63	1.95	92.0	0.7
		1.33	2.35	6.9	10.8
THF	20	2.70	0.19	2.0	3.0
		2.60	0.66	3.3	6.3
		2.45	1.07	10.0	3.4
		2.38	1.60	13.0	3.9
		2.25	1.59	14.2	3.5
		2.17	1.55	5.5	8.9
		2.15	1.90	10.5	5.7
		2.05	2.28	42.2	1.7
		1.92	2.58	73.1	1.1

where χ is the free-energy interaction parameter between any two components, the subscripts m, s, and p refer to monomer, solvent, and polymer, respectively; $\beta = \chi_{ms} - \chi_{sp} (V_m/V_s)$, where V_s is the solvent molar volume; $\Delta G_{\ell c}$ is the free-energy change upon conversion of 1 mole of liquid monomer to 1 base-mole of liquid amorphous polymer of infinite chain length, a is a constant which ideally should coincide with $\phi_m{}^0$. Assuming $a = \phi_m{}^0$ and $\chi_{mp} = 0.3$
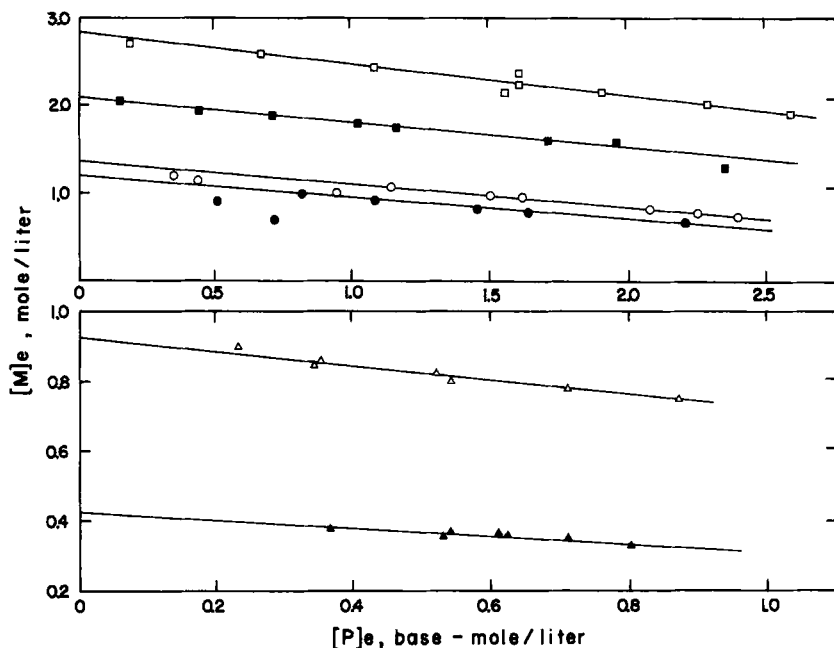
FIG. 1. Dependence of equilibrium monomer concentration on polymer concentration at various temperatures: (□) 20°C; (■) 15°C; (○) 5°C; (●) 0°C; (△) -5°C; (▲) -20°C. Polymerizations at -20 and -5°C were initiated with sodium-naphthalene complex, the rest of the studies were carried out with potassium as initiator.

for the present range of polymer concentrations [17], β and $- (\Delta G_{\ell c}/RT)$ may be computed by making use of Eq. (4) and (5).

Results of these calculations are shown in Table 3, where these are also compared with those obtained for the α-methylstyrene-THF [9] system. It may be noted that for the p-isopropyl-α-methylstyrene-THF system, function β, which is the sum of two parameters describing the solvent-monomer and solvent-polymer interactions, increases regularly with increase in polymerization temperature. Under same conditions of temperature increase for the α-methylstyrene-THF system, the trends in the increase of β values are not regular and are less pronounced.

In Table 3 are also listed the values of χ_{ms} as a function of temperature. These have been computed by making an assumption that χ_{sp} for the two systems being compared is the same, i. e., 0.3.

TABLE 2. Experimental Values of A, B, V_m, V_p, $\phi_m{}^0$, and b at Various Temperatures

Temperature (°C)	A (mole/liter)	- B (mole/basemole)	V_m (liter/mole)	V_p (liter/basemole)[a]	$\phi_m{}^0$	- b
-20	0.425	0.110	0.175	0.150	0.074	0.128
- 5	0.926	0.202	0.177	0.152	0.164	0.237
0	1.206	0.246	0.178	0.153	0.214	0.287
5	1.367	0.255	0.179	0.153	0.244	0.298
15	2.088	0.277	0.180	0.154	0.376	0.324
20	2.821	0.348	0.181	0.155	0.510	0.405

[a]Volume computed for a 24% solution of the polymer in the monomer.

TABLE 3. Values of β, χ_{ms}, and $\Delta G_{\ell c}/RT$ Deduced from Eqs. (4) and (5) for Values of χ_{mp} and χ_{sp} = 0.3

Temperature (°C)	p-Isopropyl-α-methylstyrene			α-Methylstyrene[a]		
	- β	- χ_{ms}	- $\Delta G_{\ell c}/RT$	- β	- χ_{ms}	- $\Delta G_{\ell c}/RT$
-20	1.60	0.93	3.10	1.21	0.73	3.69
- 5	1.41	0.74	2.03	1.30	0.82	2.83
0	1.34	0.67	1.66	1.14	0.66	2.36
5	1.18	0.51	1.38	0.94	0.46	1.93
15	0.69	0.02	0.52	0.96	0.48	1.33
20	0.63	-0.04	0.13	0.97	0.49	1.06

[a]Data of Ivin and Leonard [9].

The χ_{ms} values in the temperature range of -20 to 5°C are comparable in the two systems. However at 15 and 20°C these values are higher for the p-isopropyl-α-methylstyrene-THF system. The reason why in the two system the χ_{ms} values between -20 to 5°C are closer

to each other whereas β values showed more pronounced differences, lies in the values of V_m/V_s ratios (1.6 for α-methylstyrene-THF and 2.25 for p-isopropyl-α-methylstyrene-THF). One may recollect that V_m/V_s ratio is an important factor in the calculation of χ_{ms} from the β values $[\beta = \chi_{ms} - \chi_{sp} (V_m/V_s)]$.

The values of $\Delta G_{\ell c}/RT$ in both systems increase with increasing temperature (Table 3), and the values under same conditions are higher for the p-isopropyl-α-methylstyrene-THF system. Higher values of $\Delta G_{\ell c}/RT$ may be attributed to the p-substitution in the monomer used in the present studies.

In the work of Hopff and Lussi [8] the values of ΔH_{ss} and ΔS_{ss} for different phenyl-substituted styrenes were identical. In the present studies, $\Delta H_{\ell c}$ and $\Delta S_{\ell c}$ may be computed from the plots of $\Delta G_{\ell c}/RT$ versus $1/T$ and compared with those for α-methylstyrene to evaluate the change due to p-substitution in the phenyl ring. In Fig. 2 such a plot is shown, and one notes that except the value at -20°C all other values fall on a straight line. It is worth mentioning here that, in the case of the α-methylstyrene-THF system [9] also, the value at -20°C did not lie on the line for the relationship valid for all other temperatures. The values of $\Delta H_{\ell c}$ and $\Delta S_{\ell c}$ for the present system were computed to be -12.7 ± 0.5 kcal/mole and -43.1 ± 1.6 cal/deg-mole. Under the same conditions, these values for the α-methylstyrene-THF system were -10.9 kcal/mole and -34.5 cal/deg-mole. These differences in the values of $\Delta H_{\ell c}$ and $\Delta S_{\ell c}$ may be attributed to the p-substitution in the phenyl ring.

In Fig. 2 is also shown a plot of $\ln [M]_e$ versus $1/T$ in order to determine the ceiling temperature T_c of p-isopropyl-α-methylstyrene. It may be seen that $\ln [M]_e$ vs. $1/T$ yields a linear plot, and at 37°C the value of $[M]_e$ approaches that of the maximum possible $[M]_0$. Thus 37°C is the T_c value for the monomer, and at this temperature ϕ_p should be zero, at least theoretically.

Another point of interest in this study is the value of $\Delta G_{\ell c}/RT$ at T_c, obtained on extrapolating the curve for $\Delta G_{\ell c}/RT$ versus $1/T$. The theoretical relationship between $\Delta G_{\ell c}/RT$ and the monomer concentration in Eq. (5) may be rewritten for T_c by arranging $\phi_p = 0$, $a = 1$, and $\phi_m = 1$. Thus
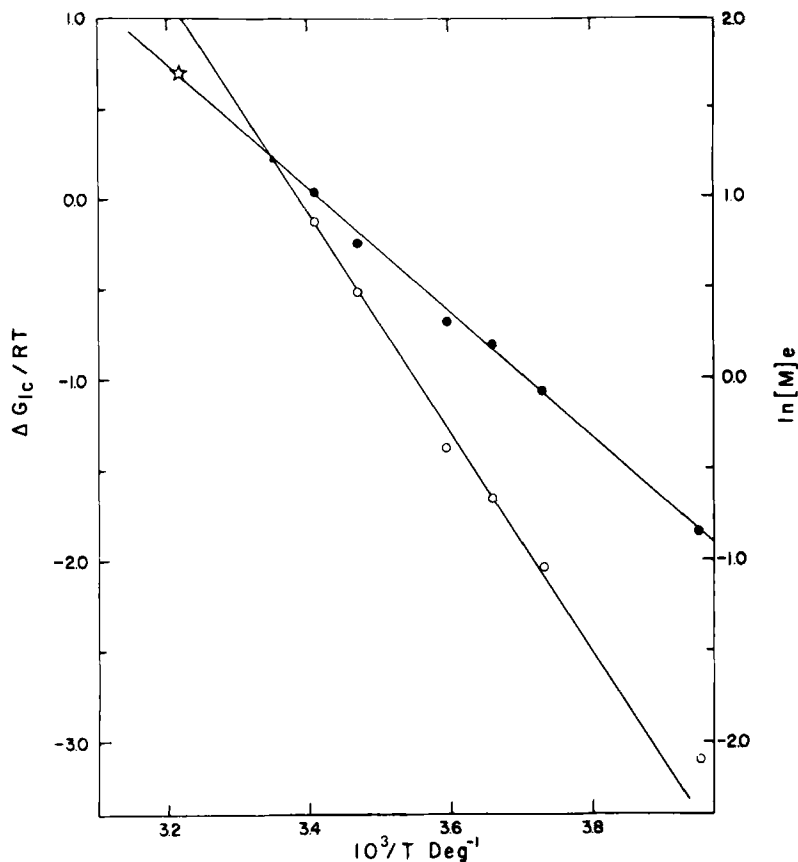
FIG. 2. Variation of $\Delta G_{\ell c}/RT$ with $1/T$ and $\ln [M]_e$ versus $1/T$ for the polymerization of p-isopropyl-α-methylstyrene in THF: ($\circ$) - $\Delta G_{\ell c}/RT$; and ($\bullet$) $\ln [M]_e$ (*) denotes $[M]_e$ maximum (calculated).

$$\Delta G_{\ell c}/RT = 1/\chi_{mp} \tag{6}$$

The value of χ_{mp} at low temperatures has been taken as 0.3. It is not known whether this value changes with temperature, and, if it does, in which sense. If one retains this value of $\chi_{mp} = 0.3$ at T_c,

the maximum value of $\Delta G_{\ell c}/RT$ is about 0.7. Making use of this value of $\Delta G_{\ell c}/RT$ a ceiling temperature of $33°C$ was determined for p-isopropyl-α-methylstyrene from Fig. 2. The difference of $4°C$ in the two T_c values either arises from the wrong value of β or may reflect on the magnitude of error on T_c one may expect from these two methods.

ACKNOWLEDGMENTS

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