Modification of the Solution Properties of Polystyrene in Cyclohexane by the Incorporation of Small Amounts of Foreign Groups

Terminal polar groups are reported in the literature to affect the solution properties of polystyrene. Hydroxyl end groups are claimed to produce association in hydrocarbon solvents[1] and butylmercapto[2] and carboxyl[3] groups to increase the theta temperature in cyclohexane. More recently, association in cyclohexane has been claimed for polystyrene containing short (1%) center blocks of butadiene.[4] In order to prepare comb-polystyrenes we have modified several polymers by the random incorporation of small amounts of polar groups. This was found to affect their solution properties in cyclohexane. No association was found. As cyclohexane is a very good solvent for diene polymers, incorporation of short diene sequences seems unlikely to provoke association. Two polymers of this type were therefore prepared and examined in cyclohexane.

Experimental. The preparation of lightly chloromethylated polystyrenes ($C4bbCH_2Cl$, $C3bbCH_2Cl$) followed the procedure described by Pepper.[5] Some of those polymers were further modified by changing the chlorine atom to an acetate group ($C5bbCH_2Ac$, $C3bbCH_2Ac$). Potassium acetate in the presence of a crown ether was used to achieve this substitution. Details will be reported in a later publication. The starting polystyrenes were sharp distribution samples prepared by *sec*-butyllithium initiation in benzene. Gel permeation chromatography elution patterns before and after modification showed no change in distribution during the process. The block copolymers of styrene, SBS-1, and SIS-1 containing very short center blocks of butadiene and isoprene, respectively, were also produced by *sec*-butyllithium initiation in benzene. They were prepared sequentially allowing at least 24 h between successive additions of monomer. Measurements of optical density at 330 nm during the process showed that the characteristic absorption of polystyryllithium disappeared rapidly on the addition of the diene and returned within experimental error to its initial value after the second styrene addition. Accidental termination was therefore negligible. Polymers were terminated with methanol and isolated by conventional means. The techniques used have been adequately described on previous occasions.[6–9] Light-scattering, GPC, osmotic pressure, and viscosity measurements were carried out as before.[10–12]

Results. The characterization of the block copolymers is summarized in Table I. GPC traces are shown in Figure 1. The polymers have a slightly wider molecular weight distribution than comparable homopolystyrenes caused perhaps by the slowness of the crossover reaction between the isoprenyl anion pair and styrene. There is no evidence of abnormally high molecular weights in cyclohexane and the intrinsic viscosities in both cyclohexane and toluene are within experimental error equal to those expected for homopolystyrenes of the same molecular weight. The $\overline{M}_n$ values in toluene are slightly lower than the $\overline{M}_w$ values in cyclohexane but this is caused entirely by the polydispersity as confirmed by an $\overline{M}_w$ measurement of SBS-1 in toluene. It was found to be 155 000, actually slightly higher than in cyclohexane but within experimental error identical. A Zimm plot for SBS-1 in cyclohexane at 35 °C is shown in Figure 2. A Zimm plot cannot be constructed for SIS-1 which is of lower molecular weight since the variation in intensity over angle and concentration is only 2%. A small positive virial coefficient (2.2×10^{-5} ml mol g^{-2}) is observed at 35 °C about one-tenth that calculable from ref 4 ($\sim 3 \times 10^{-4}$ ml mol g^{-2}). The latter value is in fact hardly compatible with an associating system being characteristic of a polymer in a moderately good solvent.

Table I
Characterization of Styrene–Diene Block Copolymers

Polymer	$\overline{M}_n$(tol)	$\overline{M}_w$(CH)	$[\eta]$tol	$[\eta]$CH[a]
SBS-1	143 000	151 000	0.597	0.326
SIS-1	28 100	31 000		0.144

[a] At 35 °C, the effect of temperature is quite small. SBS-1 has $[\eta] = 0.313$ at 31 °C ($A_2 = 0$).

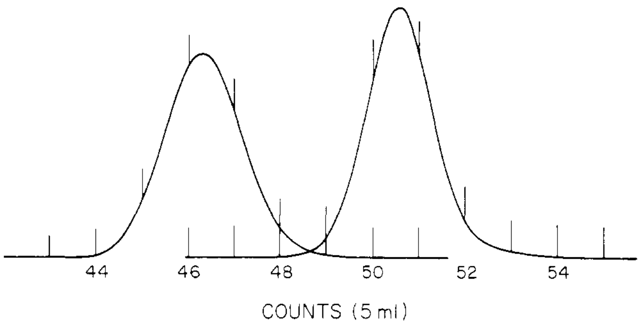

Figure 1. GPC elution patterns of polymers SBS-1 (left) and SIS-1 (right) in toluene at 35 °C; 3-ft columns of nominal pore size 3×10^6, 10^6, 5×10^5, 6.5×10^4, 2.5×10^4, 8.5×10^3, 2.5×10^3, 500, 60 Å.

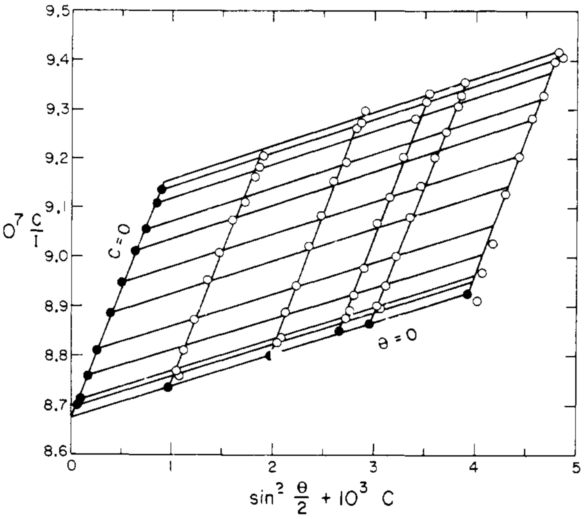

Figure 2. Zimm plot of polymer SBS-1 in cyclohexane at 35 °C (Fica-50 instrument).

The randomly modified polystyrenes have negative second virial coefficients in cyclohexane at 35 °C. The temperatures at which $A_2 = 0$ are shown in Table II. Again in no case was any evidence obtained for association in solution. The theta temperatures of the whole group of polymers can be above or below 35 °C but the deviation correlates with the nature of the extraneous groups. Poly(vinyl acetate) is insoluble in cyclohexane so θ is increased by incorporation of acetate groups whereas this solvent is better for diene polymers resulting in a decrease of θ. It seems unlikely that $\Delta\overline{S}_1$ would be changed appreciably by such small modifications in polymer structure and hence $\Delta\theta$ is mainly caused by changes in $\Delta\overline{H}_1$. Figure 3 shows the plot of A_2 against $(1 - \theta/T)$ for several of the polymers having $M \sim 150\,000$. No change in the initial slope around $(1 - \theta/T) = 0$ is observed within experimental error indicating little change in $\Delta\overline{S}_1$. If no change in $\Delta\overline{S}_1$ is assumed, $\Delta\theta$ is a very sensitive measure of small overall changes in $\Delta\overline{H}_1$. The results here would require, assuming $\Delta\overline{H}_1$ is an additive function of the mole or volume fractions of normal and ab-

Table II
Theta Temperatures of Some Modified Polystyrenes in Cyclohexane

Polymer	Mol % added groups	Location	θ, °C	$\overline{M}_w \times 10^{-5}$
SBS-1	1.77	Center	31.8	1.51
SIS-1	1.57	Center	32.0	0.31
C4bbCH_2Cl	1.47	Random	38.2	1.38[b]
C3bbCH_2Cl	3.88	Random	44.0	1.57
C5bbCH_2Ac	1.77	Random	43.2	1.53
C3bbCH_2Ac	3.88	Random	49.3	1.58
CObb3c[a]	1.93	Random	41.0	1.58

[a] A fraction of a random styrene–vinyl acetate copolymer described in ref 12. [b] $\overline{M}_w$ of the original polystyrene (unmodified) was 134 000.

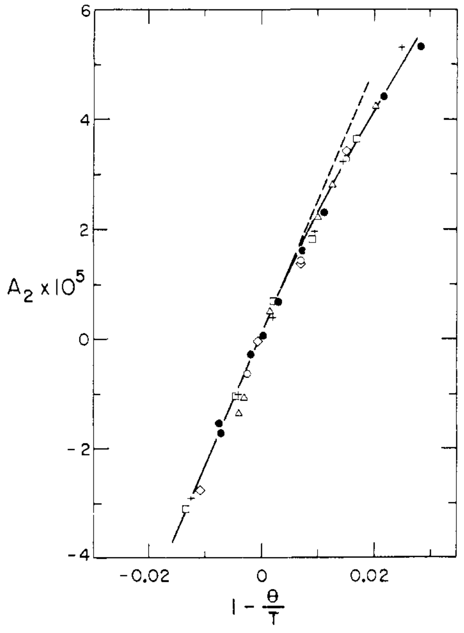

Figure 3. Second virial coefficient in cyclohexane as a function of temperature: (●) C_4bb; (◇) C_4bbCH_2Cl; (○) C_3bbCH_2Cl; (□) C_3bbCH_2Ac; (+) C_5bbCH_2Ac; (△) SBS-1.

normal groups, that the heat of dilution is roughly twice as great for chloromethylated groups and about half as great for diene groups as for normal polystyrene units.

Depression of the theta temperature ($A_2 = 0$) has been noted for comb[13,14] and star polystyrenes.[11,15] This effect has been attributed to the high segment density in such polymers.[16] The present work indicates the possibility of another effect connected with changes in $\Delta\overline{H}_1$ at the junction points. The latter points have the properties of a foreign group whose nature depends on the coupling reaction used. This effect could be important particularly at low molecular weights. The presence of unreacted chloromethyl groups in incompletely coupled comb polystyrenes would affect θ but in the opposite direction to that normally observed in comb polymers. In one case[11] up to 1% of isoprene units were present at the junction point of some star polystyrenes to facilitate the coupling reaction. The θ depression was observed however in the absence of isoprene and in addition the maximum effect on θ would be 2° in the polymer of lowest molecular weight where the percentage of isoprene reached 1%.

Acknowledgment. The authors wish to thank Dr. A. Garton for the preparation of polymer SBS-1.

References and Notes

(1) Q. A. Trementozzi, R. F. Steiner, and P. Doty, *J. Am. Chem. Soc.*, **74,** 2070 (1952).
(2) D. McIntyre, J. H. O'Mara, and B. C. Konouck, *J. Am. Chem. Soc.*, **81,** 3498 (1959).
(3) H. Ohnuma, K. Igi, T. Kotaka, and H. Inagaki, *Bull. Chem. Res. Kyoto*, **44,** 123 (1966)..
(4) L. J. Fetters and M. Morton, *Macromolecules*, **7,** 552 (1974).
(5) K. W. Pepper, H. M. Paisley, and W. A. Young, *J. Chem. Soc.*, 4097 (1953).
(6) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38,** 1891 (1960).
(7) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **42,** 2884 (1964).
(8) S. Bywater and D. J. Worsfold, *J. Organomet. Chem.*, **10,** 1 (1967).
(9) A. Garton and S. Bywater, *Macromolecules*, **8,** 694 (1975).
(10) J. E. L. Roovers and S. Bywater, *Macromolecules*, **8,** 251 (1975).
(11) J. E. L. Roovers and S. Bywater, *Macromolecules*, **7,** 443 (1974).
(12) J. E. L. Roovers, *Polymer*, **16,** 827 (1975).
(13) D. Decker, *Makromol. Chem.*, **125,** 136 (1969).
(14) F. Candau and P. Rempp, *Eur. Polym. J.*, **8,** 757 (1972).
(15) J. G. Zilliox, *Makromol Chem.*, **156,** 121 (1972).
(16) F. Candau, P. Rempp, and H. Benoit, *Macromolecules*, **5,** 627 (1972).

J. E. L. Roovers and S. Bywater*
Chemistry Division
National Research Council of Canada,
Ottawa, Canada

Received April 26, 1976

Radiation-Induced Pyrolysis of Poly(α-methylstyrene). Formation of 1,1,3-Trimethyl-3-phenylindane by an Ionic Chain Reaction

We wish to report an ionic chain reaction which occurs during the radiation-induced pyrolysis of poly(α-methylstyrene) and results in the formation of a dimer, 1,1,3-trimethyl-3-phenylindane (TMPI). Pyrolysis of poly(α-methylstyrene) under vacuum, where the decomposition by a radical chain reaction is important, was studied long ago, and it is known that below about 400 °C polymer decomposes almost completely into monomer.[1] The present investigation on the radiation-induced pyrolysis is concerned with the decomposition by ionic reactions initiated by irradiation at high temperature. Poly(α-methylstyrene) powder was evacuated at a pressure of 10^{-6} mm for 24 h in a Pyrex tube equipped with a cold finger and then sealed.[2] The sample was heated at 200 °C under irradiation of ^{60}Co γ rays (the dose rate, 9.2 $\times 10^5$ rad/h), and the volatile products were collected in the cold finger which was cooled with liquid nitrogen and protected by a leadblock from radiation. The products both trapped in the cold finger and remaining in the irradiated polymer were analyzed with a gas chromatograph using a Apiezon L column.

It was found that the products almost exclusively consist of monomer and a dimer, TMPI, while the only product detected was monomer when heated at 200 °C in the absence of radiation. The dimer was identified by its nmr spectrum [$\tau(CCl_4)$ 2.91 (9 H, m), 7.56 (1 H, d, $J = 13$ Hz), 7.89 (1 H, d, $J = 13$ Hz), 8.39 (3 H, s), 8.71 (3 H, s), 9.00 (3 H, s)] and mass spectrum (M^+ at m/e 236). The dimer produced was also contained in the irradiated polymer and the amount of the dimer remaining in the polymer was comparable with that trapped in the cold finger, while the monomer almost completely passed over into the cold finger. The total yield of the dimer was proportional to the irradiation time in the range studied, up to 3 h. The G value of the dimer was 34, and such a high yield suggests that it is formed by a chain reaction. When the polymer was irradiated at room temperature or heated at 200 °C after irradiating at room temperature, the yield of TMPI was much smaller, G(TMPI) < 1. Thus, it is indicated that the chain reaction generating TMPI occurs at high temperature under irradiation.