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Solution Polymerization of Styrene

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Summary

Polymers were obtained by free-radical solution polymerization of styrene, carried out by continuous feed-type polymerization. Molecular weights were determined by gel-permeation chromatography, light scattering, and osmotic pressure and viscosity measurements. A study of molecular structures indicated that polymerizations of styrene conducted in solution at relatively low temperatures and to a low degree of conversion can result in varying degrees of branching when certain initiating radicals are present.

Free-radical polymerization of styrene carried out at elevated temperatures and to a high degree of conversion may lead to branched structures (1). The amount of branching increases with temperature and with initiator concentration. Lower temperature bulk polymerizations of styrene, on the other hand, were shown to yield linear molecules (2), particularly when carried to a low degree of conversion. This paper reports a study into the molecular structures of polystyrene formed by free-radical solution polymerization where continuous feed-type polymerization conditions (3,4) were employed.

RESULTS AND DISCUSSION

Five homopolymers of styrene (polymers I-V) were prepared. The conditions for polymerization are summarized in Table 1. Reproducibility of preparative procedure was tested by repeating preparations of polymers I, III, and V. Molecular weights of the second preparations and the yields fell within 5% of the original

TABLE I
Conditions Used for Preparation of Polymers

Polymer	Initiator	Concn. of initiator in monomer, %	Time of addition, hr	Solvent	Polym-erization temp., °C	Conver-sion, %
I	Benzoyl peroxide	2.0	2.0	Toluene	110–112	70.0
II	Benzoyl peroxide	2.0	0.5	Benzene	79–80	6.9
III	Benzoyl peroxide	2.0	1.5	Benzene	79–80	24.5
IV	<i>t</i> -Butylperoxy isopropyl carbonate	2.0	1.5	Benzene	79–80	10.0
V	<i>t</i> -Butylperoxy isopropyl carbonate	1.0	1.0	Benzene	79–80	10.0

ones. However, the data presented in this paper are based only on results from original preparations.

Polymer VI is an anionically prepared, narrow-molecular-weight-distribution polystyrene from the National Bureau of Standards, No. 705. Polymer VII is a wide-molecular-weight-distribution polystyrene prepared by thermal bulk polymerization; also from the National Bureau of Standards, No. 706. The two polymers were used for the purpose of comparison.

Table 2 shows molecular weights of these polymers as determined by light scattering, gel permeation, osmotic pressure, and viscosity measurements. It also shows the molecular weight distributions, the g values, and the average branch points per molecule calculated from g values, based on the relationships of g to viscosities for branched and linear chains. The Zimm and Kilb (5) relationship of g to intrinsic viscosities was used:

$$g^{1/2} = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$$

where $[\eta]_{\text{linear}}$ was calculated from the equation

$$[\eta] = 9.773 \times 10^{-5} \bar{M}^{0.73}$$

as reported by McCormick (6). To accomplish this, \bar{M}_w 's obtained by light scattering were used in the above equation.

TABLE 2
Molecular Weights of the Polymers

Polymer	M_w , lt. scat.	M_w , GPC	M_n , osm. pr.	M_n , GPC	M_v	M_w/M_n , lt. scat/ osm. pr.	M_w/M_n , GPC
I	23,200	21,100	12,100	10,700	19,000	1.92	1.97
II	38,900	37,300	25,200	21,000	37,500	1.54	1.78
III	44,500	42,300	27,700	16,000	41,100	1.61	2.64
IV	204,500	113,600	84,600	51,500	162,000	2.42	2.20
V	227,500	149,400	101,000	53,800	185,700	2.25	2.78
VI	179,300	166,700	170,900	124,500	—	1.05	1.34
VII	257,800	231,000	136,500	101,300	244,700	1.89	2.28

Such treatment of light-scattering data to obtain $[\eta]_{\text{linear}}$ was described by Krause and Cohn-Ginsberg (7), who applied it to studies of poly(methyl methacrylate) and is based on an approach of Cohn-Ginsberg et al. (8).

Whole polymers were used in the study rather than fractions. Such use of whole polymers results in overestimation of g values when obtained from ratios of end-to-end distances, and in underestimation when obtained from the ratios of intrinsic viscosities. Thus the values of g shown in Table 3 are relatively crude estimates. Similar approaches, however, were used by other investigators (9) who accepted them as being significant enough to allow comparison. The average number of branch points per molecule was obtained with the aid of Zimm-Stockmayer calculations for trifunctional branch units with branches of random length (10).

TABLE 3
Degree of Branching as Estimated from g Values

Polymer	$[\eta]_{\text{linear}}$, calcd.	$[\eta]$, exptl.	g	Average branch points
I	0.15	0.13	0.750	3.60
II	0.219	0.213	0.945	0.60
III	0.242	0.228	0.889	1.25
IV	0.736	0.620	0.710	4.45
V	0.795	0.685	0.743	3.75
VII	0.871	0.838	0.942	0.85

Calculations based on g values indicate that polymers I, IV, and V may be branched and that polymers II, III, and VII are linear. This is confirmed by GPC data, judging from the work of Benoit and co-workers (11), who demonstrated from GPC studies of linear and branched polystyrenes that the hydrodynamic volume of the solvated molecule is the basic parameter in gel permeations. This volume, they feel, is related to the radius of gyration and can be calculated from the relationship (12)

$$[\eta] = \Phi[(\bar{r}^2)^{3/2}/M]$$

This led them to conclude that a polymer of higher molecular weight, but branched, would appear in gel-permeation chromatography at the same count as its linear homolog of lower molecular weight. As a result, for branched polymers the \bar{M}_w as measured by GPC will be substantially lower than the \bar{M}_w as measured by light scattering. Such a difference can be observed from comparison of weight-average molecular weights for polymers I, IV, and V as determined by light scattering and by gel-permeation chromatography (Table 2).

NMR spectra were then used to study these polymers further. The theoretical ratio of aliphatic/aromatic hydrogens in a linear polystyrene should be 3:5. Any branching, should it occur by the mechanism of chain transferring to the more labile aliphatic protons, would result in ratios of less than 3 aliphatic to 5 aromatic hydrogens. On the other hand, any branching occurring by the mechanism of chain transferring to the ring would result in higher aliphatic/aromatic ratios. Kirchner (13) demonstrated that thermal polymerization of styrene at 127.3°C may result in transferring to ring ortho positions. These ratios were measured, therefore, from the spectra of these polymers by integrating the respective areas under the curves (14). Accuracy of NMR data for such determinations would, of course, be a limiting factor in any utility of such information. If an accuracy of $\pm 2\%$ is possible, then variation in a ratio of 3:5 is 0.600 ± 0.012 . This may allow a qualitative picture. Table 4 shows the data. It was gathered on two different instruments at two different laboratories to establish the degree of reproducibility and is recorded in the manner in which it was reported. The results shown are averages of five scans for each

TABLE 4
Average Ratios of Aliphatic to Aromatic Hydrogens

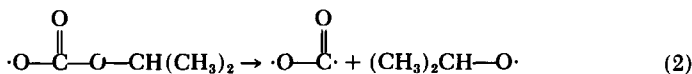
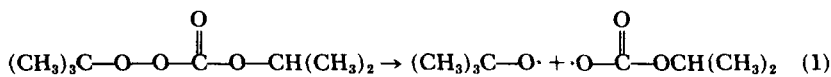
Polymer	Simon Research Lab., Varian A-60	Stauffer Chemical Co., Varian A-60-A	Stauffer Chemical Co., Varian A-60-A
I	2.866/5.000	2.896/5.000	—
II	2.97/5.00	—	—
III	2.995/5.000	—	—
IV	3/5	3.04/5.00	3.05/5.00
V	2.999/5.000	—	—
VI	3.004/5.000	—	—
VII	3.007/5.000	—	—

determination. It was found that the average deviation for each determination was much less than 2%.

The data presented here are believed by us to be insufficient to establish utility of NMR spectra, if any, for determination of branching. But it allows some interesting comparisons and is therefore presented. Based on the above considerations, it would appear that the NMR data also suggest that polymer I is branched.

Polymers II to V were prepared at 80°C. The amount of thermal polymerization which would occur at this temperature and in the period of time the reaction was carried out appears to us to be very low, judging from the study of thermal polymerization of styrene carried out by Schulz and Husemann (15). Also, there is no specific information in the literature to suggest that transferring to the ring occurs in free-radical styrene polymerization reactions which are not thermally initiated. The NMR data indicate 3:5 ratios of aliphatic/aromatic hydrogens for these polymers. If these data are to be believed, then they suggest linear structures from all four polymers and contradict the results obtained from g values and from GPC studies on polymers IV and V. This might, perhaps, be explained if polymers IV and V were star-shaped. In a star-shaped structure, the number of aliphatic hydrogens which were replaced by branches may actually be small, so that deviation from a 3:5 ratio may not be within the detectable range of the method. It must be noted here that polymers IV and V were prepared at relatively low temperature and carried to a low degree of conversion. And, as the

chain-transferring coefficient for styrene is low, one would expect linear structures. Yet the data indicate that this is not the case. Perhaps an explanation might be found in the nature of the initiator. If the radicals from decomposition of *t*-butylperoxy isopropyl carbonate are active enough for an occasional transfer to the polymer backbone, then indeed branching may be expected. This peroxide is believed (16) to decompose by the mechanism of peroxy oxygen cleavage accompanied by loss of CO₂ from the carbonate radical:



The *t*-butoxy radical was shown by Smets and co-workers (17) to be insufficiently active for reactions with polystyrene. It must therefore be discarded as the potential source of transfer. The isopropoxy radical is capable of undergoing two types of reactions: elimination of a hydrogen radical and subsequent formation of acetone (major) (1) and abstraction of hydrogen and formation of isopropyl alcohol (minor) (2). The second reaction, although minor, may perhaps be responsible for the formation of branches. Furthermore, the fact that this reaction is minor may result in a limited number of branches or a star-shaped molecule.

Whether one might also speculate that rather than star-shaped structures, cyclizations occurred, with the resultant effects upon *g* values, is a matter of conjecture. These polymerizations were not conducted in high dilutions. In fact, upon completion of all reactions, the ratio of the monomer-polymer mixtures to those of the solvents was 3:1. This makes us doubt the likelihood of cyclization, although we are not prepared to rule it out on firm grounds. The effect of cyclization on the end-to-end distance of molecules and subsequent behavior in gel-permeation chromatography is not clear.

Preparation of polymer I was carried to a high degree of conversion in the presence of an initiator and the reaction conducted at higher temperature, so some branching might be expected. It is significant to observe, however, that no branching was indicated from this data for polymer VII, which was formed thermally and

in bulk, with the conversion carried to 37%, but without any initiator. This agrees with the known behavior of the growing polystyrene radical (18).

EXPERIMENTAL

Polymer Preparation

Polymers I through V were prepared in three-necked, round-bottom flasks equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel. One hundred and twenty-five grams of the solvent was placed into the flask and 325 g of freshly distilled monomer containing the initiator was added dropwise at a constant rate to the refluxing solvent under a nitrogen atmosphere. Upon completion of the addition, the reaction mixture, a clear solution, was quenched with methanol, causing the polymer to precipitate as a white powder, and then added to a large excess of the alcohol. The precipitated polymer was redissolved in methyl ethyl ketone and reprecipitated with methanol, washed with fresh methanol, and dried in a vacuum oven for 24 hr at 100°C and 0.5 mm Hg.

All analytic data presented on molecular weights are an average of three determinations. Molecular weight distribution by gel-permeation chromatography (19,20) was obtained by using three 4-ft gelled polystyrene columns (Waters Associates), pore sizes 10^5 , 10^4 , and 10^3 Å, with tetrahydrofuran as the solvent. Weight-average molecular weights were obtained, using a Brice-Phoenix light-scattering photometer in toluene solvent.

Number-average molecular weights were determined with the aid of a Mechrolab high-speed membrane osmometer in cyclohexanone using S & S, U.O., very dense gel cellophane membranes. Viscosity-average molecular weights were obtained by measuring viscosities in toluene at 25°C in an Oswald-Fenske viscometer, using a $[\eta] = 9.773 \times 10^{-5} M_e^{0.73}$ relationship (6).

Nuclear magnetic resonance data were obtained using Varian A-60 and A-60-A high-resolution spectrometers at 60 Mc. Determinations were carried out on CDCl_3 solutions of the polymers at room temperature, with cps filter bandwidth, rf field of 0.2 mg, sweep time of 250 and 50 sec, sweep width of 500 cps and spectrum amplification of 8.0 and 3.2. The integral amplification was 80. All data presented are an average of five scans.

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Zusammenfassung

Polymere wurden mittels einer kontinuierlich vor sich gehenden Radikal-Lösungspolymerisation von Styrol dargestellt. Die Molekulargewichte wurden mittels Gelpermeationschromatographie, Lichtstreuung Osmotischen Druck und Viskositätsmessungen ermittelt. Eine Untersuchung der molekularen Strukturen zeigt, dass die Polymerisation von Styrol, wenn sie in Lösung bei relativ niedriger Temperatur bei geringen Umsatzgraden durchgeführt wird, in verschiedenen Verzweigungsgraden resultieren kann, wenn gewisse Starterradikale vorhanden sind.

Résumé

On a obtenu des polymères du styrolène par polymérisation radicalaire libre en solution, effectuée en alimentation continue. On a déterminé les masses moléculaires par chromatographie de perméabilité des gels, par diffusion de la lumière, par des mesures des pressions osmotiques et de viscosité. Une étude des structures moléculaires indique que la polymérisation du styrolène faite en solution à une température relativement basse et un degré de conversion bas, peut donner des branchement variables lorsque certains radicaux amorceurs sont présents.

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