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Glass Transition of Oligostyrene with Different End Groups

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ABSTRACT: Oligostyrenes having butyl groups at both ends, a butyl group at one and a proton at the other, and protons at both ends were prepared. The oligomers obtained were separated into fractions from monomer to octamer by the combined use of vacuum distillation and gel permeation chromatography (GPC). The purity of each fraction was characterized by GPC. The monomer and dimer having butyl groups at both ends were found to crystallize; melting and premelt crystallization were detected by differential scanning calorimeter (DSC). All the oligomer fractions and the monomer became glassy when quenched from the molten state. The glass transition temperatures (T_g's) of the oligomers having the same number of main chain segments were similar in spite of the difference in molecular weight (M_n). Thus, the values of the constants in the equation of $T_g=A-B/M_n$ (where A and B are constants) varied depending on the type of sample in the range of molecular weight up to 600. This fact indicates that the molecular motion of the end groups cancels out the effect of increasing molecular weight.

KEY WORDS Oligostyrene / End Group / Fractionation / Molecular Weight / Glass Transition / Differential Scanning Calorimetry /

The molecular weight at which polymolecularity appears in polymers has received much attention. The molecular weight dependence of physicochemical properties of polymers has been discussed in a large number of reports. In particular, the variation in glass transition temperature T_g with the molecular chain length is well established for various kinds of amorphous polymers.[1-7] The value of T_g for a given polymer varies remarkably in the low molecular weight region and attains a characteristic temperature at a certain molecular weight. Oligometric materials are considered to be a suitable model for studying the variation of T_g and also the appearance of the polymolecularity. In spite of the importance of oligomers, few papers have been concerned with the relation between T_g and chain length in the low molecular weight region.[8,9] Uebbereiter and Kanig[8] synthesized styrene oligomers by bulk polymerization and separated them into different molecular weight fractions. They observed T_g by dilatometry and explained the observed relationship between T_g and molecular weight by introducing the self-plasticization effect of the end groups.

Recently, Cowie[10] systematically studied the transition temperature of various kinds of oligomers and replotted all the available data for T_g against the molecular weight. He found a characteristic molecular weight at which T_g varied discontinuously.

In these studies, oligomer purity is not specified, but T_g is known to be affected by molecular weight distribution. Samples having narrow molecular weight distribution exhibit high T_g, even in the high molecular weight region.

In this study, we prepared two kinds of fractionated styrene oligomers having different end groups. The dimer and the trimer of oligostyrene containing double bonds in the main chain were also examined as a reference.

EXPERIMENTAL

Sample Preparation

Three kinds of styrene oligomers were used in this experiment. The chemical structures of the samples are as follows:

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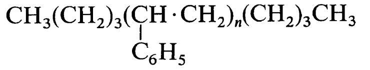
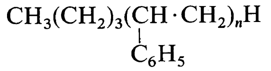
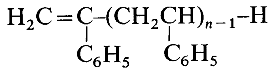
(I)

$CH_3(CH_2)_3(\underset{C_6H_5}{\underset{|}{CH}}\cdot CH_2)_n(CH_2)_3CH_3$

(II)

$CH_3(CH_2)_3(\underset{C_6H_5}{\underset{|}{CH}}\cdot CH_2)_nH$

(III)

$H_2C=\underset{C_6H_5}{\underset{|}{C}}-(CH_2\underset{C_6H_5}{\underset{|}{CH}})_{n-1}-H$

Sample I has butyl groups at both ends, sample II has a butyl group at one end and a proton at the other, and sample III has protons at both ends. Samples I and II were prepared by ionic polymerization according to the reported procedure.[11,12] The as-polymerized samples were obtained as mixtures of dimer to 20-mer. Several samples having different number-average molecular weights were prepared by controlling the synthesis conditions.

Fractionation of the mixture of oligomers was carried out using a gel permeation chromatograph (GPC) of Nihon Bunseki Model LC-08 equipped with a 20 mm diameter column.

At the same time, several column systems which enabled separation of the sytrene oligomers were developed at our laboratory. The details of the fractionation were similar to those reported previously.[13] A dimer and/or trimer rich fraction was also obtained by vacuum distillation, but it is separated into completely pure fractions, judging from the GPC diagram. Accordingly, the distilled samples were refractionated by GPC to obtain pure samples.

The structures of the dimer and the trimer were characterized by a high resolution NMR of Japan Electric Co.'s, JEOL-C60HL. Detailed characterization of samples I and II is found in previous reports.[11,14]

Samples II was prepared by Mr. Sekiguchi (Nihon University) who distilled thermally decomposed polystyrene.[15]

Measurements

Differential Scanning Calorimetry (DSC). A differential scanning calorimeter (Perkin-Elmer DSC II) equipped with a low temperature environmental chamber was used. The environment of the sample holder was kept water-free and a stream of helium was made to flow through the apparatus during the heating and cooling runs. The sample weight was 3—5 mg and the scanning rate was 5—20 K min^{-1}.

Gel Permeation Chromatography (GPC). A gel permeation chromatography (Toyo Soda HLC-801A) was used for analysis of the molecular weight. Each GPC peak was related to the number of main chain segments using a known dimer and trimer as the reference. The fractionation was carried out by a GPC of Nihon Bunseki (LC-08).

GPC curves were analyzed by a Curve Resolver (du Pont Model 310), assuming that each GPC peak was gaussian. The purity of the sample was calculated from the area of the resolved peaks.

Microscopy. A polarized light microscope (Leitz model ORTHOLUX) equipped with a heating stage and camera was used.

RESULTS AND DISCUSSION

Figure 1 represents the GPC chromatograms of the original samples I and II. The repeating number of the main chain segments, n, in each oligomer is indicated by a numerals in the figure. The chromatograms of the fractions obtained by vacuum distillation of the sample II are also shown in the figure. The dimer-rich fraction II-a contains the trimer, and the trimer-rich fraction II-b contains the dimer. These chromatograms show that a pure fraction was difficult to obtain by distillation alone. The sample became appreciably purer when the distilled fractions II-a and II-b were further separated by the

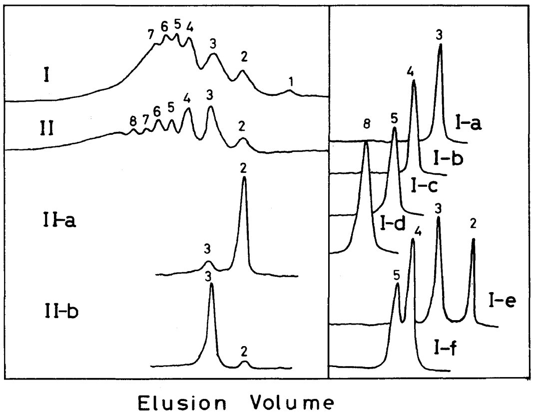


Figure 1. Gel permeation chromatograms of oligostyrenes: I, II, original samples I and II; II-a, II-b, distilled fractions of sample II; I-a, I-b, I-c, I-d, resolved fractions of sample I by GPC; I-e, I-f, mixtures of sample I.

Table I. Molecular weights, purities, and T_g's of oligostyrenes used in this experiment

		Sample I (○)[a]				Sample II (●)[a]				Sample III (□)[a]		(△)[a]	
Number of main chain segement (n)	(Number of end group) /n (M_e)	M_n	(Molecular weight of end group) /M_n (W_e)	Purity % (Impurity % of mixed n-mer)	T_g K	M_n	(Molecular weight of end group) /M_n (W_e)	Purity % (Impurity % of mixed n-mer)	$T_g{}^b$ K	M_n	Purity % (Impurity % of mixed n-mer)	$T_g{}^b$ K	$T_g{}^c$ K
1	2	218	0.52	99 (1, 2-mer)	174	162	0.36			104		(146)	
2	1	322	0.35	99 (1, 3-mer)	200	266	0.22	98 (2, 3-mer)	196	209	96 (1, 3-mer)	197	195
3	0.67	426	0.27	91 (1, 4-mer 4, 1-, 2-mers)	232	370	0.16	98 (2, 4-mer)	229	312	87 (13, 3-mer)	231	233
4	0.50	530	0.22	82 (18, 5-mer)	253	474	0.12	90 (10, 5-mer)	246				247
5	0.40	634	0.18	78 (22, 6-mer)	264	578	0.10	One peak	260				
6	0.33	738	0.15	90 (10, 7-mer)	275	682	0.09	One peak	268				
7	0.29	842	0.13	One peak	282								
8	0.25	946	0.12	One peak	289								284
		2.0×10^3		One peak	295	1.3×10^3		One peak	283				
		2.8×10^3		One peak	297	2.0×10^3		One peak	288				
		4.0×10^3		One peak	304								

[a] (○), (●), (□), and (△), symbols in the figure.

[b] T_g, T_g measured at the heating rate of $20\,\mathrm{K\,min^{-1}}$.

[c] T_g, ref 8.

GPC. The right hand part of Figure 1 shows the fractions separated by GPC. The resolution of the two peaks becomes more and more difficult with increasing molecular weight since the resolution factor of the column decreases with increasing molecular weight. As shown in the chromatograms of the original samples, the peaks were distinguished up to 8-mer. Oligomers having a higher molecular weight than 8-mer were difficult to detect precisely by GPC. Accordingly, samples having a higher molecular weight than that 8-mer were evaluated from the number-average molecular weights, M_n calculated from the elution number of GPC chromatograms.

The samples, the number of main chain segment, molecular weight and purity etc. are listed in Table I.

The monomer and dimer having butyl groups at both ends (sample I) crystallized gradually when the samples were kept in a refrigerator over a month. Flexible, long grass-like crystals of monomer were observed under a polarized light microscope (Photo. I). From the color of the polaized light, the molecular axis was found to be aligned along the longitudinal direction of the crystal. The peak temperature of the melting in DSC curve of the crystal was detected as the endotherm at 305 K at a heating rate of 10 K min^{-1}, as shown in Figure 2.

The crystal of the dimer grown on the heating stage of the microscope at room temperature was plate-like. The peak temperature for the melting was detected at 319 K in the DSC curve, as can be seen from Figure 2. A small exothermic deviation observed before melting peak is attributed to pre-melt crystallization, and indicates that rearrangement of the imperfect part of the crystal takes place before melting. By using X-ray diffractometry, Morimoto[16] found a periodical order of 17—18 Å in the oligostyrene having an average-molecular weight of 600. He suggested that the oligostyrene formed a smectic liquid crystal phase because the length 17—18 Å corresponds to the chain length of the extended molecule. Other photographs (not shown here) as well as the presence of the pre-melt crystallization observed in the DSC curve suggest that the oligomer molecule was extended and arranged in a longitudinal direction. All the oligomer fractions and the styrene monomer became glassy when quenched from the molten state to temperatures lower than T_g.

Typical DSC curves of oligostyrene fractions (sample I) taken at the heating rate of 20 K min^{-1} are shown in Figure 3. A typical dip of the base-line is clearly observed for these oligomer glasses. The T_g is defined as the point at which the extension of the base-line intersects the line tangent to the maximum slope of the endothermic deviation. The T_g's thus evaluated from DSC curves are presented in Table I.

The heating rate dependence of the T_g of oligomers exhibited a trend similar to that of polystyrene. The temperature difference between the

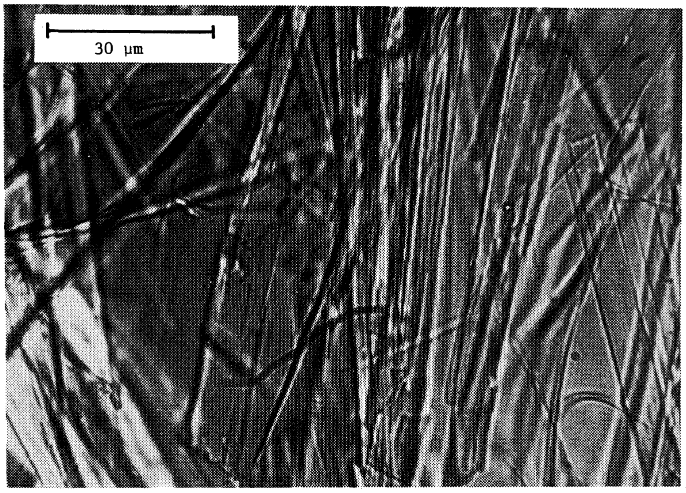


Photo I. Polarized light micrograph of styrene monomer having butyl groups at both ends (sample I). Temperature, 290 K.

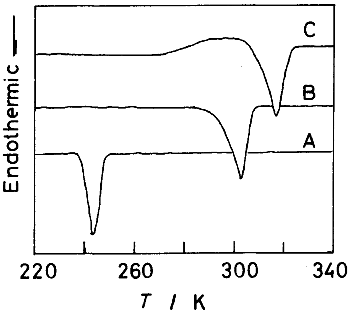
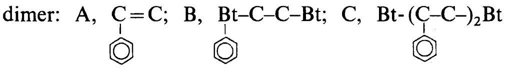


Figure 2. DSC curves of crystalline monomers and dimer: A, C=C; B, Bt-C-C-Bt; C, Bt-(C-C-)$_2$Bt


$$\mathrm{A,\ \underset{\displaystyle C_6H_5}{C}{=}C;\quad B,\ \underset{\displaystyle C_6H_5}{Bt{-}C}{-}C{-}Bt;\quad C,\ Bt{-}(\underset{\displaystyle C_6H_5}{C}{-}C{-})_2Bt}$$

Heating rate, 10 K min^{-1}.

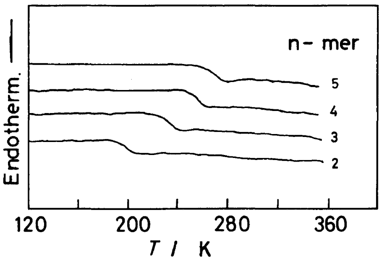


Figure 3. DSC curves of glassy oligostyrenes of sample I. Numerals indicate the number of main chain segments, n.

T_g's measured at 20 K min^{-1} and those exptrapolated to the zero heating rate was about 6—8 K for the dimer to 8-mer.

The T_g's of the three samples listed in Table I are plotted against the molecular weight, M_n, in Figure 4. The T_g's increase almost linearly with M_n up to about 600 and thereafter increase more slowly. Those for dimers and trimers do not fall on the same line, but the three lines converge for M_n above 600.

Figure 5 shows T_g plotted against the reciprocal of M_n, where roman numerals show the samples and arabic numerals the number of main chain segments. The T_g's of dimers having different end groups are almost identical, in spite of the large difference in molecular weight. The T_g's of the dimers, for example, were observed within a temperarure range from 196—200 K while molecular weight ranged from 209—322. The T_g's of trimer show a similar tendency, but the temperature range from 229—232 K and the molecular weights from 312—426. The three lines intersect at the T_g of 260 K which corresponds to the inflection point where the rate of increase in T_g changes in Figure 4. This T_g corresponds to a molecular weight of 600.

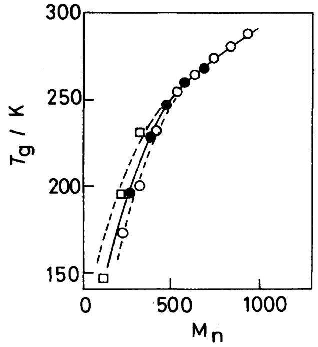


Figure 4. Relationship between T_g and M_n: ○, sample I; ●, sample II; □, sample III.

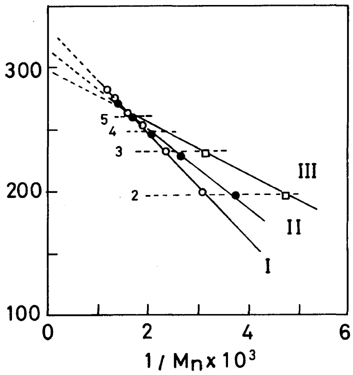


Figure 5. Relationship between T_g and $1/M_n$: I, sample I; II, sample II; III, sample III. Numerals indicate the number of main chain segments, n.

Our data conform to the well-established relation between T_g and molecular weight:

$$T_g = A - B/M_n \tag{1}$$

But A and B vary with the sample. Equation 1 for the samples I and II as are follows,

$$T_g = 332 - 4.3 \times 10^4/M_n \tag{2}$$

$$T_g = 316 - 3.2 \times 10^4/M_n \tag{3}$$

If eq 1 is applied to the sample III whose data are insufficient for accurate determination of A and B, $A = 300$ and $B = 2 \times 10^4$ can be obtained as tentative

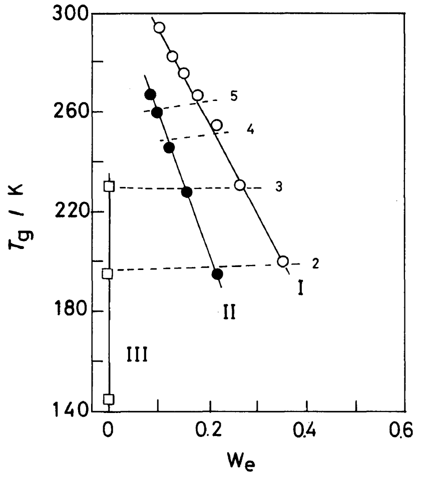


Figure 6. Relationship between T_g and W_e [=(molecular weight of end group)/M_n]: I, sample I; II, sample II; III, sample III. Numerals indicate the number of main chain segments, *n*.

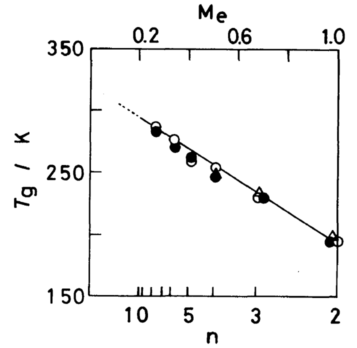


Figure 7. Relationship between T_g and *n* (number of main chain segments) and M_e [=(number of end group)/*n*]. Symbols are shown in Table I.

values. The constants *A* and *B* for samples I, II, and III vary and *B* is high compared with that calculated by Boyer.[17]

The fact that T_g of *n*-mer does not change despite the large difference in the molecular weight can be seen clearly in Figure 6, where T_g is plotted against the molecular weight fraction of the end groups, W_e, to the total molecular weight. The T_g's obtained for different samples are found on separate lines, while the number of segments, *n*, are on similar T_g lines. The values of T_g for the samples I and II exptrapolated to $W_e=0$ is in agreement with the temperature at which a discontinuity was found in the plot of T_g against the number of carbon atoms in the chain.[10] It is clear from Figures 4, 5, and 6, that the T_g's of *n*-mers are identical despite the difference in molecular weight, especially in the low molecular weight region.

The results presented in Figures 5 and 6 allow us to conclude that the T_g values plotted against the number of chain segments, *n*, should fall on a straight line. In fact, Uebbereiter and Kanig[8] have already found the same for bulk-polymerized samples, although the end groups were not characterized. All reported values,[7,8] together with those reported here are plotted in Figure 7. The value of M_e [=(number of end groups)/*n*] is also plotted on the abscissa. All the data points are well fitted by a single curve. Uebbereiter and Kanig consider that the end group function as a self-plasticizer in styrene oligomers.

If we replace the M_n in eq 1 with the number of main chain segments, we can expect to obtain general constants. We modified eq 1 to eq 4 for comparison with the reported data.[10]

$$1/T_g = A' + B'/n \qquad (4)$$

The calculated values of $A' = 2.90 \times 10^{-3}$ and $B' = 4.16 \times 10^{-3}$ accord reasonably well with those obtained previously.[10]

Summing up the results shown in Figures 6 and 7, it can be said that T_g's of oligostyrenes are governed by the number of main chain segments rather than the size of end groups. In other words, a linear relationship independent of the end groups holds between the number of chain segments and T_g in the case of oligostyrenes.

If only the surface of phenomenon were considered, the above results might contradict themselves. However, if the self-plasticizing effect of the end group mentioned by Uebbereiter and Kanig is interpreted as a local relaxation of the end group, *i.e.*, if the local movement of end groups already start at a temperature lower than T_g, the end group motion cannot be the factor affecting the main chain motion near the glass transition temperature. For explaining what occurs in the molecules of styrene oligomers, Photo. I gives the idea that molecules carrying the same number of phenyl groups should array and aggregate together despite the motion of large end groups. Hence, the ordering of the main chain or the stacking of the phenyl group may be most important in considering the main chain motion of oligostyrene.

REFERENCES

1. T. G Fox and P. J. Flory, *J. Polym. Sci.*, **14**, 315 (1954).
2. R. B. Beevers and E. G. T. White, *Trans. Faraday Soc.*, **56**, 744 (1960).
3. R. B. Beevers, *J. Polym. Sci.*, *A*, **2**, 5257 (1964).
4. E. V. Thompson, *J. Polym. Sci., A-2*, **4**, 199 (1966).
5. J. M. G. Cowie and P. J. Toprowski, *Eur. Polym. J.*, **4**, 621 (1968).
6. J. M. G. Cowie and S. J. Bywater, *J. Polym. Sci., C*, **30**, 85 (1970).
7. J. M. G. Cowie, *Eur. Polym. J.*, **9**, 1041 (1973).
8. K. Uebbereiter and G. J. Kanig, *J. Colloid Sci.*, **7**, 569 (1952).
9. K. Uebbereiter and U. Rohde-Liebenau, *Macromol. Chem.*, **48**, 164 (1961).
10. J. M. G. Cowie, *Eur. Polym. J.*, **11**, 297 (1975).
11. M. Iguchi, R. J. Ranson, and M. Gordon, *Br. Polym. J.*, **5**, 33 (1973).
12. T. Altares, D. P. Wyman, and V. R. Allen, *J. Polym. Sci.*, *A*, **2**, 4533 (1964).
13. H. Hatakeyama and T. Hatakeyama, *Mokuzai-gakkaishi*, **23**, 228 (1977).
14. S. Fujishige and N. Ohguri, *Macromol. Chem.*, **176**, 233 (1975).
15. T. Kuroki, T. Ogawa, Y. Sekiguchi, K. Saito, and T. Ikemura, *Nihon Kagaku Zasshi*, **11**, 1717 (1977).
16. S. Morimoto, *Nihon Kagaku Zasshi*, **91**, 182 (1970).
17. R. Boyer, *Macromolecules*, **7**, 142 (1974).