

Effect of Short-Chain Polymer on Scission of Long-Chain Polymer in Solution by High-Speed Stirring

AKIHIKO NAKANO* and YUJI MINOURA, *Department of Chemistry, Research Institute for Atomic Energy, Osaka City University, Sugimotocho, Sumiyoshi-ku, Osaka, Japan*

Synopsis

The effect of short-chain poly(methyl methacrylate) (PMMA) ($P_v = 950$) on scission of long-chain PMMA ($P_v = 6150$) in solution by high-speed stirring was investigated by measuring changes in $[\eta]$ and GPC, stirring at $30,000 \pm 500$ rpm at $30^\circ \pm 5^\circ\text{C}$ benzene solutions containing the above two polymers at several concentrations and at various mixing ratios. It was found that the scission of long-chain PMMA was small or a little suppressed by addition of short-chain PMMA. The scission-suppressing effect of the coexisting polymers depended on the chain length. The longer the chain, the larger the effect. It was also found that the rate constant of scission, k , in Ovenall's equation had a certain significance in polymer systems with the same MWD but no significance in those with different MWDs.

INTRODUCTION

The authors have been studying the effect of solvent, concentration, and so on, on the scission of several kinds of polymer in solution by high-speed stirring.^{1,2} It was found from the results that the rate of scission was high and the degree of polymerization reached by prolonged stirring was low for every solvent at low concentration (0.04% w/v) and vice versa at high concentration (2.00% w/v),¹ that concentration dependence of scission was large for good solvents but small for poor ones,¹ and that at high-concentration polymer chains were broken relatively more easily in poor solvent,^{1,2} while at low concentration they were broken more easily in good ones.¹ When the results are considered synthetically, it is difficult to explain the scission of polymer chains by high-speed stirring by the theory that it is caused by the interaction, especially entanglement, between polymer molecules. It seems to be rather more reasonably explained by the velocity gradient formed between polymer chains and solvent molecules. The role of cavitation in such degradation processes as ultrasonics or high-speed stirring has been studied by many investigators. Even if the cavitation plays a decisive role, the authors consider that a further question may arise why it can rupture bonds of polymer molecules. In this work, the effect of the short-chain polymer on the scission of the long-chain polymer was studied by stirring at high speed the solutions containing both easily breakable long-chain polymers and short-

* Present address: Wireless Research Laboratory, Matsushita, Electric Industrial Co., Ltd. 1006, Kadoma, Osaka, Japan.

chain polymers under limiting degree of polymerization which were expected not to degrade, in order to know the detailed mechanism of the scission and the relation of scission to the interaction between polymer chains.

EXPERIMENTAL

Materials

The long-chain poly(methyl methacrylate) (abbreviated Hi-PMMA) for mechanical scission was the same as that used in the previous paper.¹ Intrinsic viscosity $[\eta]$ in benzene at 30°C was 2.48 dl/g. Viscosity-average degree of polymerization \bar{P}_v was 6,150 (molecular weight 615,000).

Delpet 70H supplied by Asahi Kasei was used as short-chain PMMA (Lo-PMMA), which was considered to be lower than the limiting degree of polymerization; $[\eta] = 0.48$ dl/g, $\bar{P}_v = 950$, molecular weight 95,000.

The solvent was benzene purified by the usual method. Benzene is considered to be a medium good solvent for PMMA, the θ temperature for benzene-PMMA solution being -223°C .

Experiment

The benzene solutions (200 ml) containing both Hi-PMMA and Lo-PMMA at various concentrations and ratios were prepared and stirred at $30^\circ \pm 5^\circ\text{C}$ at a speed of $30,000 \pm 500$ rpm. Polymers were recovered after stirring for a given time by evaporating the solvent with warm air. The high-speed mixer and stirring procedure were the same as described previously.^{1,3}

Intrinsic viscosities of polymers were measured in benzene at $30^\circ \pm 0.02^\circ\text{C}$ by an Ubbelohde viscometer. As the molecular weight distribution varies

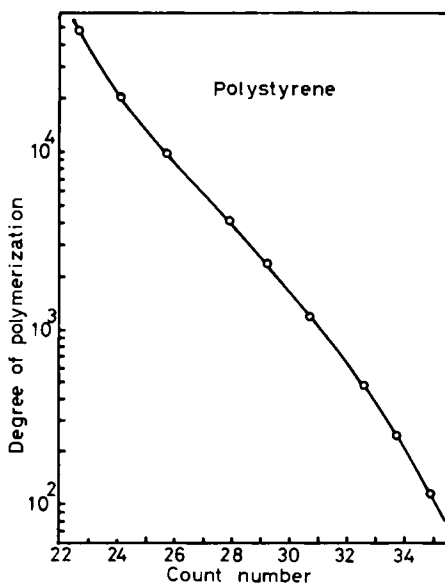


Fig. 1. Calibration curve obtained by polystyrene standards.

owing to scission of chains during stirring, it is, of course, most appropriate to estimate the number-average degree of polymerization, \bar{P}_n , for calculation of the number of scissions. But the viscosity-average degree of polymerization, \bar{P}_v , was used here for the sake of convenience. The discussion below was therefore restricted within the range which could be allowed. The equation⁴ used for the calculation of \bar{P}_v is as follows:

$$\bar{P}_v = 2,200 \times [\eta]^{1.13} \quad (1)$$

A Waters Associates GPC Model 200 was used for measurement of gel permeation chromatography. It was operated at 25–30°C using tetrahydrofuran (THF) as solvent. The column sequence was 10⁷, 10⁶, 10⁵, 10⁴ Å. A flow rate of 1 cc/min was maintained. Injections were for 2 min. Concentrations were kept at about 0.5% in all cases. Polystyrene standards by Pressure Chemicals were used to obtain a calibration curve. In Figure 1 is shown the calibration curve showing the relationship between count number and degree of polymerization for polystyrene.

The number of scission per molecule, limiting degree of polymerization, and rate constant of scission for Ovenall's⁵ eq. (2) were calculated by the method described in the previous paper³:

$$\left. \begin{aligned} \frac{dB_i}{dt} &= k(P_i - P_1)n_i && \text{(when } P_i > P_1) \\ \frac{dB_i}{dt} &= 0 && \text{(when } P_i \leq P_1) \end{aligned} \right\} \quad (2)$$

where dB_i/dt is the rate of scission of molecules of degree of polymerization P_i ; n_i is the number of such molecules; k is the rate constant of scission; and P_1 is the limiting degree of polymerization below which molecules cannot be degraded.

RESULTS AND DISCUSSION

Scission of Hi-PMMA by High-Speed Stirring in the Presence of Lo-PMMA

Benzene solutions, 200 ml, containing both Hi-PMMA and Lo-PMMA at various concentrations and ratios as shown in Table I were prepared and stirred by the high-speed mixer at 30,000 ± 500 rpm for a given time. Intrinsic viscosities of polymers recovered after stirring are shown by the symbol (+) in Figures 2 and 3.

The $[\eta]$ values of the mixture of Hi-PMMA and Lo-PMMA which had been separately stirred for a given time at corresponding concentrations were calculated by use of Flory's⁶ eq (3) for $[\eta]$ of the mixture. They are shown by the symbol (O) in Figures 1 and 2:

$$[\eta]_{A+B} = \alpha[\eta]_A + \beta[\eta]_B \quad (3)$$

where $[\eta]_A$, $[\eta]_B$, and $[\eta]_{A+B}$ are $[\eta]$ of polymer A, polymer B, and the mixture of polymers A and B, respectively; and α and β are the weight fractions of polymers A and B in the mixture, respectively.

TABLE I
Sample Solutions and Their Rate Constants of Scission and Limiting Degrees of Polymerization

Sample solution	Content of Hi-PMMA, % w/v	Content of Lo-PMMA, % w/v	Wt. ratio of Hi-PMMA to Lo-PMMA	Initial degree of polymerization	P_1 (Limiting degree of polymerization)	k (Rate constant of scission) $\times 10,^6 \text{ min}^{-1}$
a	0.040	0	1/0	6,150	2,020	28.2
b	0.040	0.013	1/0.33	4,850	2,000	47.3
c	0.040	0.040	1/1	3,470	1,660	41.6
d	0.040	0.120	1/3	2,020	1,420	58.6
e	0	0.040	0/1	950	950	0
A	0.200	0	1/0	5,810	2,820	21.0
B	0.200	0.066	1/0.33	4,460	2,240	20.8
C	0.200	0.200	1/1	3,300	1,990	36.7
D	0.200	0.600	1/3	1,970	1,460	47.7
E	0	0.200	0/1	950	950	0
F	0.080	0.080	1/1	3,250	1,590	37.1

It was found that when the solutions containing only Lo-PMMA were stirred, the recovered polymers scarcely showed change in $[\eta]$, whether the concentration was high (Fig. 1) or low (Fig. 2). That is, scission of polymer chain was scarcely observed. The results were as expected, since polymers below the limiting degree of polymerization which was found from the previous experiment was selected for the study. When the solutions containing only Hi-PMMA were stirred, $[\eta]$ of the recovered polymer was rapidly decreased at the initial stage of stirring but decreased slowly at a later stage. In this case, the final $[\eta]$ was lower when the polymer was stirred at a low concentration than at a high concentration. When the solutions containing both Hi-PMMA and Lo-PMMA were stirred, the recovered polymers showed intermediate degradation curves between the above two curves for only Hi-PMMA and for only Lo-PMMA, nearly corresponding to their mixing ratios.

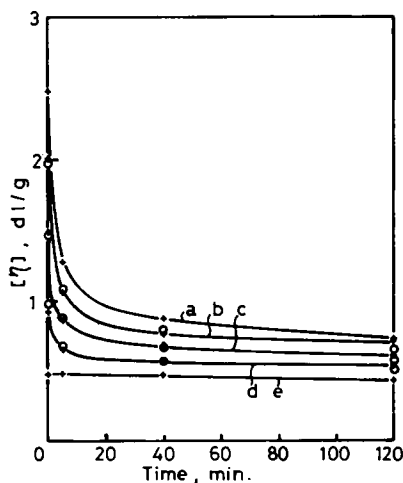


Fig. 2. Degradation of polymer mixture of Hi-PMMA and Lo-PMMA by high-speed stirring (Hi-PMMA 0.04% w/v). Refer to Table I.

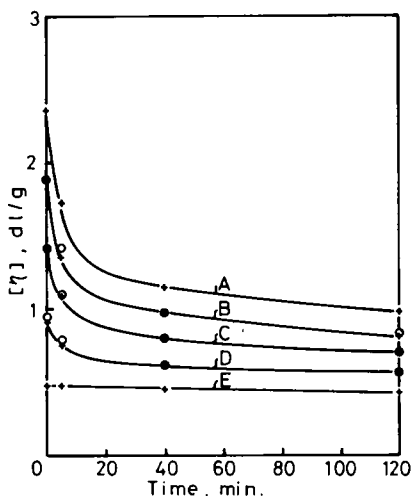


Fig. 3. Degradation of polymer mixture of Hi-PMMA and Lo-PMMA by high-speed stirring (Hi-PMMA 0.200% w/v). Refer to Table I.

In order to know whether there is an effect or not of Lo-PMMA on the scission of Hi-PMMA when a solution containing a mixture of easily breakable Hi-PMMA and hardly breakable Lo-PMMA was stirred at a high speed, and to know the extent of the effect, it might be necessary to recover thoroughly all fragments formed from only Hi-PMMA in the solution after stirring and to compare the intrinsic viscosity of the fragments with the one of fragments formed when the solution containing only Hi-PMMA was stirred. However, it is impossible for the same kind of polymer. Therefore, the comparison was tried between $[\eta]_{\text{obs}}$, the intrinsic viscosity of the polymer mixture of Hi-PMMA and Lo-PMMA which had been stirred at mixed state, and $[\eta]_{\text{calc}}$, one of Hi-PMMA and Lo-PMMA which had been stirred separately. $[\eta]_{\text{calc}}$ was not measured but calculated by eq. (5) described above. Whether the concentration of Hi-PMMA was high or low, both of them agreed with each other as shown in Figures 1 and 2, excepting that $[\eta]_{\text{obs}}$ was a little larger than $[\eta]_{\text{calc}}$ after 120 min of stirring at 0.04% w/v. Hi-PMMA seems to have been broken as if it had been given no effect by Lo-PMMA. When Hi-PMMA solutions are stirred alone at 0.04% w/v and at 0.200% w/v, respectively, more violent chain scission was observed for the former as seen by the comparison of curves a and A in Figures 2 and 3. Long-chain poly(methyl methacrylate) seems not to be affected in its scission by the presence of short-chain poly(methyl methacrylate) below the limiting degree of polymerization, although it is prevented from breaking by the presence of the same-chain length polymers.

Change in Molecular Weight Distribution by High-Speed Stirring

Measurement of GPC was carried out in order to confirm the above observations by another method and to obtain the knowledge on the change in molecular weight distribution (MWD).

In Figures 4–8 are shown the normalized GPC curves measured for the polymers recovered after stirring for a given time from the solutions contain-

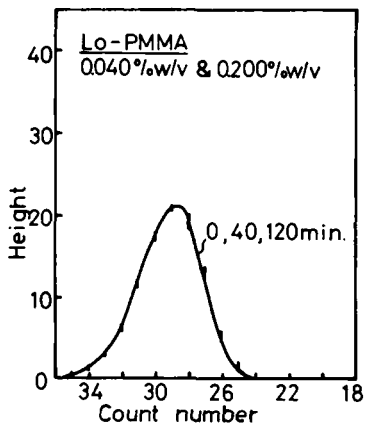


Fig. 4. GPC of short-chain polymer (Lo-PMMA) before and after stirring.

ing only Lo-PMMA at 0.04% w/v and at 0.200% w/v, the ones containing only Hi-PMMA at the above concentrations, and the ones containing the equivalent amount of Hi-PMMA and Lo-PMMA at the above concentrations. In Figures 7 and 8, the area of GPC for the mixtures is twice as large as for Hi-PMMA or Lo-PMMA alone. When Lo-PMMA was stirred alone, it scarcely gave any change in the GPC even after stirring, regardless of concentration as shown in Figure 4.

In the case of solutions containing Hi-PMMA, the GPC shifted to the left with stirring time, as seen in Figures 5–8. If the relationship in Figure 1 nearly similarly holds for PMMA, the results in Figures 5–8 show that long-chain molecules disappeared to form short-chain molecules and that MWD became narrow with stirring. The extent is found to be large with decreasing concentration as seen from the respective comparison between Figures 5 and 6 and between Figures 7 and 8.

The GPC curves which might be obtained for the mixture of the equivalent amount of Hi-PMMA and Lo-PMMA which had been separately stirred for the same time were calculated by their respective GPC curves. The calculated curves are shown by dotted lines in Figures 7 and 8. The observed GPC

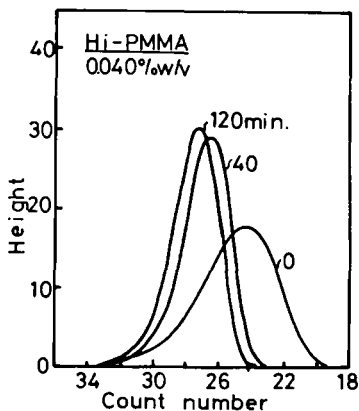


Fig. 5. Change in GPC of long-chain polymer (Hi-PMMA) with stirring at 0.04% w/v.

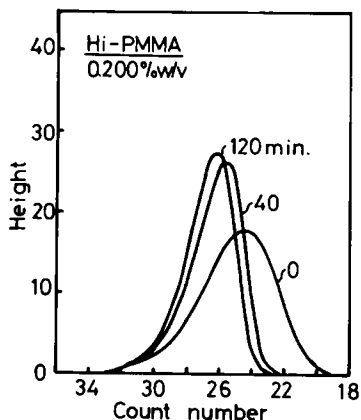


Fig. 6. Change in GPC of long-chain polymer (Hi-PMMA) with stirring at 0.200% w/v.

curves shown by solid lines for the mixture before stirring and the calculated ones nearly agreed with each other. This suggests that GPC curves after mixing can be calculated from respective GPC curves measured separately before mixing within experimental error if the mixing ratios are known. It is noted that the calculated curve for the polymer stirred for 120 min slightly shifted to the left, namely, to shorter chain length (Fig. 7) and that the peak of the curve was higher (Fig. 8). Such difference was not found for polymers stirred for 40 min, the calculated curves not being shown. The difference between observed curves (solid lines) and calculated ones (dotted lines) observed above shows that the presence of Lo-PMMA affected the scission of Hi-PMMA during stirring. Because the observed curves had more long-chain components, addition of Lo-PMMA seems to have suppressed the breakage of Hi-PMMA. But the suppressive effect is considered not to be so large as it is detected by the viscosity method.

The increase in concentration of Hi-PMMA itself suppresses the scission of Hi-PMMA, as seen from the comparison between a in Figure 2 and A in Figure 3; and, moreover the suppressive effect is considerably large. On the other

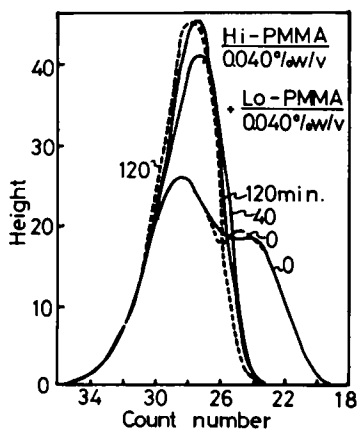


Fig. 7. Change in GPC of mixture of long- and short-chain polymers (0.04% w/v Hi-PMMA and 0.04% w/v Lo-PMMA) with stirring. Solid curve: found; dotted curve: calculated.

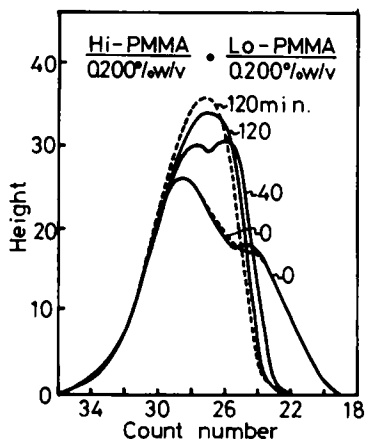


Fig. 8. Change in GPC of mixture of long- and short-chain polymers (0.200% w/v Hi-PMMA and 0.200% w/v Lo-PMMA) with stirring. Solid curve: found; dotted curve: calculated.

hand, the Hi-PMMA component in solution d was broken like that in solution a, showing much more rapid scission than solution A, though the concentration of total polymer in solution d in Figure 2 was nearly the same as in solution A in Figure 3 (more precisely, the concentration of solution d was 80% of solution A). The increase in concentration of total polymer by adding Lo-PMMA to Hi-PMMA caused little if any decrease in the scission of Hi-PMMA. In other words, the presence of long-chain polymers comparable to breaking polymers significantly suppresses the scission, while that of short-chain polymers that are not broken suppresses little. The scission-suppressing effect due to coexisting polymers depends on the chain length. It is considered that the longer the chain, the larger the effect. It is also considered that the polymers with high degree of polymerization, consequently with a large hydrodynamic volume, are easily broken by high-speed stirring but that they are resistant to flow which decreases velocity gradient and suppresses the scission of other neighboring polymers. On the contrary, the polymers below P_1 are hardly broken but may be negligibly resistant to flow which does not largely decrease velocity gradient.

Limiting Degree of Polymerization and Rate Constant of Scission for Polymers with Different MWD

The right columns in Table I show limiting degrees of polymerization P_1 and rate constants of scission k calculated for the results of various solutions. P_1 decreased, but k increased with increase in mixing ratio of Lo-PMMA at both concentrations (k was zero when only Lo-PMMA was stirred). When P_1 and k are respectively compared between two solutions containing the same ratio of Hi-PMMA and Lo-PMMA at different concentrations, that is, between two solutions with the same initial MWD, such as between a and A, b and B, and so on, it can be seen that P_1 was lower and that k was larger for lower concentration. Considering the previous results¹ that polymer chains are more easily broken with decreasing concentration, decrease in P_1 and increase in k with decreasing concentration of polymer mixture are reasonable

as a tendency; but increase in k with increasing ratio of Lo-PMMA is not reasonable, because addition of Lo-PMMA did not promote the scission of Hi-PMMA as observed above with the results of $[\eta]$ and GPC.

At first, the authors expected that k was maintained constant regardless of the mixing ratios of Hi-PMMA and Lo-PMMA on account of the small effect of the latter, or that k was increased with increasing ratio of Hi-PMMA from zero in the case of only Lo-PMMA to the value in the case of only Hi-PMMA because of increasing ratio of easily degrading polymer. However, the calculated results were quite contrary to expectations. It was found that the rate constant of scission k in Ovenall's equation has a certain significance, as it reflects the rate of scission to some extent for polymers with the same MWD, but that it sometimes becomes a false rate constant that does not reflect the actual state of scission for polymer systems with different MWDs. The estrangement from the actual state is considered to have originated from the estimation of the number of scission calculated conveniently by the viscosity-average degree of polymerization, which should have accurately been calculated by the number-average degree of polymerization, or from the fact that obtained values of P_1 and k are only approximate ones for curves of experimental number of scission versus stirring time which can not absolutely be expressed by Ovenall's equation.

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