

Effects of Solvent and Concentration on Scission of Polymers with High-Speed Stirring

A. NAKANO* and Y. MINOURA, *Department of Chemistry, Research Institute for Atomic Energy, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan*

Synopsis

The effects of solvent and concentration on scission of polymers such as poly(methyl methacrylate) (PMMA) and polystyrene (PSt) in solution by high-speed stirring were investigated. Solvents were chloroform (good), benzene (intermediate), and ethyl acetate (poor) for PMMA and methyl ethyl ketone (good), toluene (intermediate) and dioxane (poor) for PSt, respectively. Concentration was varied from 0.04 to 2% w/v. The rate of scission of polymer chains was higher and the final molecular weight was lower in a good solvent than in a poor solvent at a low concentration for both polymers, but vice versa at a high concentration except for PSt in methyl ethyl ketone. Concentration dependence of the scission was large in a good solvent but small in a poor one. Polymer chains were ruptured to lower molecular weights with decreasing concentration, regardless of kind of polymer and solvent, showing that they were more easily broken in the isolated state.

INTRODUCTION

The authors have been studying the effect of polymer concentration, solvent, stirring speed, initial degree of polymerization, and different kind of polymer on the degradation of polymers such as poly(ethylene oxide) (PEO), polystyrene (PSt), poly(methyl methacrylate) (PMMA), and polyisobutylene (PIB) in solution by high-speed stirring.¹⁻³

In the high-speed stirring of PEO in benzene at a concentration range of 2-5% w/v, intrinsic viscosity of the polymer was similarly decreased regardless of concentration of solution.¹ When a mixture of PEO and PMMA was stirred, the same degradation curves as those obtained when they were stirred separately were obtained, showing that the existence of a different kind of polymer did not affect the degradation of another polymer with each other when they were stirred at a concentration range of 2-5% w/v.³ The results (that the rate of scission of polymer chain by high-speed stirring was independent of polymer concentration and mixture ratio of two kinds of polymer) seem to show that the mechanical scission of polymer by high-speed stirring is independent of the interaction between polymer chains for the concentration range. The results obtained for the effect of solvent on the scission were consistent with the above.³ The fact that the rate of scission is decreased with expanding of polymer chain in the solvent is considered to show that the interaction between polymer chains suppresses the mechanical scission. Therefore, the authors considered that it remains as problem whether the en-

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

tanglement⁴ between polymer chains which causes the scission of chains in mastication can be the essential factor in the scission in high-speed stirring of the solution and that it is needed to furthermore investigate the effect of the interaction between polymer chains on the mechanical scission of polymer chains.

The effect of concentration of polymer solution on the scission of polymer chains by high-speed stirring has been studied by the authors,^{1,2} by Rodriguez and Winding,⁵ by Grohn and Opitz,⁶ by Johnson and Price,⁷ and by Goto and Fujiwara.^{8,9} Rodriguez et al. and Grohn et al. recognized the effect of concentration. The former stirred polyisobutylene at a high rotating speed in the concentration range of 0.5–0.16 g/dl and found that the rate of scission became zero when it was extrapolated to infinite dilution. They concluded that the polymer chains were not broken by contact only with solvent but broken by contact of a polymer chain (entanglement) with other chains. However, other investigators did not confirm the effect of concentration. It was noted the results where no effect was found were obtained for relatively high concentrations, over 1%, and that the results where the effect of concentration was recognized were obtained for lower concentrations.

In this work, the solutions containing 0.04–2% w/v of polymer in several solvents were stirred at high speed, and the effect of polymer concentration on rate constant of scission, k , and limiting degree of polymerization, P_1 , was studied. It is supposed that the interaction between polymer chains is almost absent in 0.04% w/v solution. Polystyrene and poly(methyl methacrylate) were selected because of easy availability and their different characteristics. For example, they have different glass transition temperatures. The former is prepared from α -carbon substituted vinyl monomer, while the latter from α -carbon disubstituted one. Polymer radicals formed from the former usually terminate by recombination, but the ones from the latter terminate by disproportionation. For both polymers good, intermediate, and poor solvents were selected.

EXPERIMENTAL

Polymers

Polymers for mechanical scission were spontaneously polymerized poly(methyl methacrylate) (PMMA) and polystyrene (PSt). They were purified by reprecipitation. PMMA purified showed an intrinsic viscosity $[\eta]$ of 2.52 dl/g in benzene at $30^\circ \pm 0.02^\circ\text{C}$. Molecular weight was 620,000 (degree of polymerization, P , 6,200). $[\eta]$ of PSt purified in benzene at 30°C was 2.28 dl/g. Molecular weight was 583,000 (P , 5,610). PSt of higher molecular weight was supplied by Pressure Chemical Co. as a standard monodisperse polystyrene. Nominal molecular weight was 2,000,000, and \bar{M}_w/\bar{M}_n was less than 1.30. $[\eta]$ measured by the authors was 4.66 dl/g in benzene at 30°C , and molecular weight was 1,590,000 (P , 15,300). It was used for stirring as is.

Solvents

Solvents for PMMA were chloroform, benzene, and ethyl acetate; and solvents for PSt were toluene, 1,4-dioxane, and methyl ethyl ketone (MEK). These solvents were purified by the usual method and used after distillation.

TABLE I
 θ -Temperature and Intrinsic Viscosity for Each System

| System | $[\eta]$ at 30°C, dl/g | θ -Temperature, °C |
|-------------------------|------------------------|---------------------------|
| PMMA—chloroform | 3.50 | -273 |
| PMMA—benzene | 2.80 | -223 |
| PMMA—ethyl acetate | 1.56 | -98 |
| PSt—toluene | 2.30 | -113 |
| PSt—dioxane | 2.22 | -75 |
| PSt—methyl ethyl ketone | 1.20 | -273 |

From the viewpoint of θ temperature, chloroform is the best, benzene the next best, and ethyl acetate the poorest solvent for PMMA. They represent a good, intermediate, and poor solvent, respectively. The better a solvent, the higher the intrinsic viscosity it gave for the same original PMMA.

From the viewpoint of θ temperature, MEK is the best, toluene the next best, and dioxane the poorest solvent for PSt. However, toluene gave the highest $[\eta]$, dioxane the next highest, and MEK the lowest for the same original PSt. MEK gave a lower $[\eta]$ than the expected one. In Table I are shown θ temperature¹⁰ and $[\eta]$ of original PMMA and PSt in their respective solvents at 30°C.

Apparatus for Stirring and Method of Stirring

A T.K. Homomixer of HS-M type made by Tokushu-Kika Kogyo Co., Ltd., was used as a high-speed stirrer. The stator, turbine, and vessel of the mixer were the same as those used in the previous experiment.¹

A solution containing a given weight of polymer in 200 ml of solvent was stirred in a 300-ml vessel made of stainless steel. Stirring speed was 30,000 rpm. For keeping the temperature of the solution at $30^\circ \pm 5^\circ\text{C}$ and to keep the mixer safe from harm by superheating, 5 min of stirring and 5 to 10-min pauses for cooling were alternated. After stirring for a given time, about 10 ml of stirred solution was taken out, and then stirring was continued. In case of dilute solutions less than 0.2% w/v, solutions were stirred batchwise.

Polymer Separation

Polymer solutions stirred for a given time were dried by a warm-air drier until their weights became constant.³ Infrared spectra of polymers before and after stirring were measured in the range of 4000–670 cm^{-1} . In the case of PMMA, absorption band at 1735 cm^{-1} due to carbonyl group was found to decrease little after 360-min stirring for 2% w/v solution, while in the case of PSt, the absorption band near 1740 cm^{-1} assigned to the carbonyl group was observed to slightly increase. It is considered that in the case of PSt, chain ends formed from chain scissions terminate by the addition of oxygen in the air to give carbonyl group, whereas chain ends terminate by disproportionation resulting in little change in absorption strength in the case of PMMA.

Method of Measuring $[\eta]$ and Molecular Weight

Intrinsic viscosities of recovered polymers, $[\eta]$, were all measured in benzene at $30^\circ \pm 0.02^\circ\text{C}$ using an Ubbelohde viscometer. Since the molecular

weight distribution is considered to vary owing to scission of chains during stirring, it is 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 according to custom for the sake of convenience. The equations used for the calculation of \bar{P}_v are as follows:

$$\begin{aligned}\bar{P}_v &= 2200 [\eta]^{1.13} \text{ for PMMA}^{(11)} \\ \bar{P}_v &= 1770 [\eta]^{1.40} \text{ for PSt}^{(12)}\end{aligned}$$

Rate Constant of Scission, k , and Limiting Degree of Polymerization, P_1

Rate constant of scission, k , and limiting degree of polymerization, P_1 , in Ovenall's¹³ eq. (1) for obtained results were determined by the method described in the previous paper.¹

Ovenall's rate equation

$$\left. \begin{aligned} \frac{dB_i}{dt} &= k(P_i - P_1)n_i & (P_i > P_1) \\ \frac{dB_i}{dt} &= 0 & (P_i \leq P_1) \end{aligned} \right\} \quad (1)$$

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

Effects of Concentration on Scission of PMMA and PSt in Several Solvents

Benzene solutions containing 0.04–2% w/v of PMMA and toluene solutions containing 0.04–2% w/v of PSt were prepared and stirred at a speed of 30,000 rpm. Decrease in $[\eta]$ of recovered polymer with stirring is shown in Figures 1 and 2. In all cases, the value of $[\eta]$ decreased rapidly at first and then slowly, reaching a constant value depending on the polymer and concentration of solution. It is found that the rate of decrease in $[\eta]$ increased and final $[\eta]$ decreased with decrease in concentration for both polymers. The tendency was also observed for PMMA stirred in chloroform or ethyl acetate and for PSt stirred in dioxane or MEK.

The relationships between number of scission per polymer molecule and stirring time for PMMA solution and for PSt solution are shown in Figures 3 and 4, respectively. The number of scissions per molecule, B_t/n_0 , was calculated by the equation

$$B_t/n_0 = (P_0/P_t - 1)$$

where P_0 and P_t are the degrees of polymerization before stirring and after stirring for time t , respectively. The number of scissions increased rapidly at

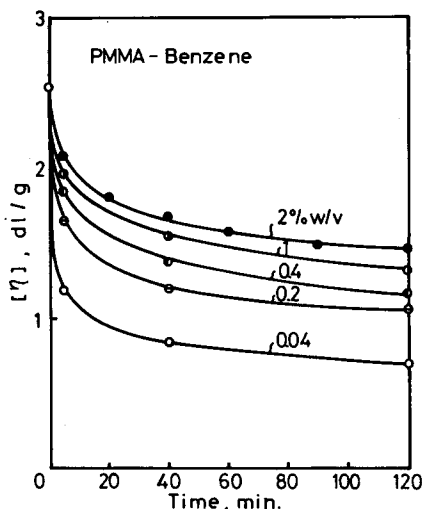


Fig. 1. Degradation of PMMA in benzene by high-speed stirring for various concentrations: (●) 2% w/v; (○) 1%; (◐) 0.4%; (◑) 0.2%; (○) 0.04%; at 30,000 rpm, 30°C.

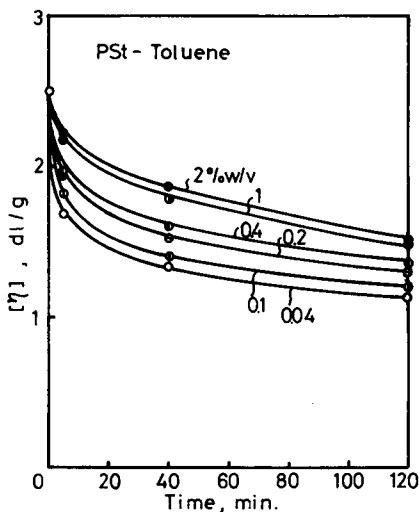


Fig. 2. Degradation of PSt in toluene by high-speed stirring for various concentrations: (●) 2% w/v; (○) 1%; (◐) 0.4%; (◑) 0.2%; (◒) 0.1%; (○) 0.04%; at 30,000 rpm, 30°C.

first and then slowly. The value of the number of scissions depended on the concentration of polymer and the solvent. In these figures, B_t/n_0 versus t calculated using the value of P_1 and k in Tables II and III below are also shown by solid lines.

Tables II and III show P_0 , P_1 , final degree of polymerization, P_∞ (degree of polymerization obtained after stirring for infinite time, $P_\infty = \frac{3}{4}P_1$), and k for PMMA and PSt, respectively. It is found that P_1 became smaller and k larger with decrease in the concentration of solution. This is discussed below.

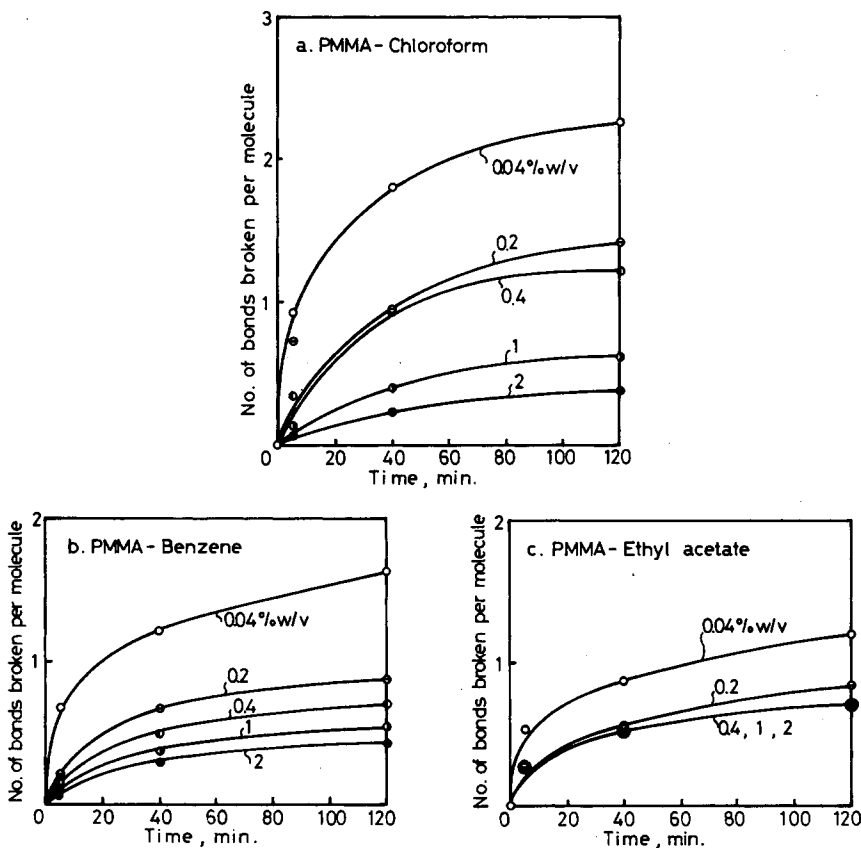


Fig. 3. Relationship between number of scission per polymer molecule and stirring time for PMMA in (a) chloroform, (b) benzene, and (c) ethyl acetate at several concentrations: (●) 2% w/v; (○) 1%; (●) 0.4%; (○) 0.2%; (○) 0.04%.

Effect of Initial Degree of Polymerization on Scission of PSt in Toluene

In order to investigate the effect of concentration of solution containing different degree of polymerization of PSt on the scission, toluene solutions containing 0.04% w/v and 1% w/v of PSt with initial degree of polymerization 15,300 were stirred, respectively. The stirring speed was 30,000 rpm. Decrease in $[\eta]$ of PSt recovered after stirring is shown in Figure 5 together with the results for PSt with initial degree of polymerization 5610. It was found that the rate of scission was higher and final $[\eta]$ was smaller for lower concentration in case of stirring of high initial degree of polymerization of PSt as well as low one. The values of P_1 and k expressing the results were calculated as follows: For 0.04% w/v: $P_0 = 15,300$, $P_1 = 3,000$, $P_\infty = 2,250$, $k = 10.8 \times 10^{-6}$. For 1.00% w/v: $P_0 = 15,300$, $P_1 = 4,100$, $P_\infty = 3,080$, $k = 4.00 \times 10^{-6}$.

Final $[\eta]$ at each concentration was expected to be the same respectively when the stirring condition, except initial degree of polymerization of PSt, was the same, even if the initial degree of polymerization, P_0 , was different. Nevertheless, the values were not the same but close after 2 hr of stirring.

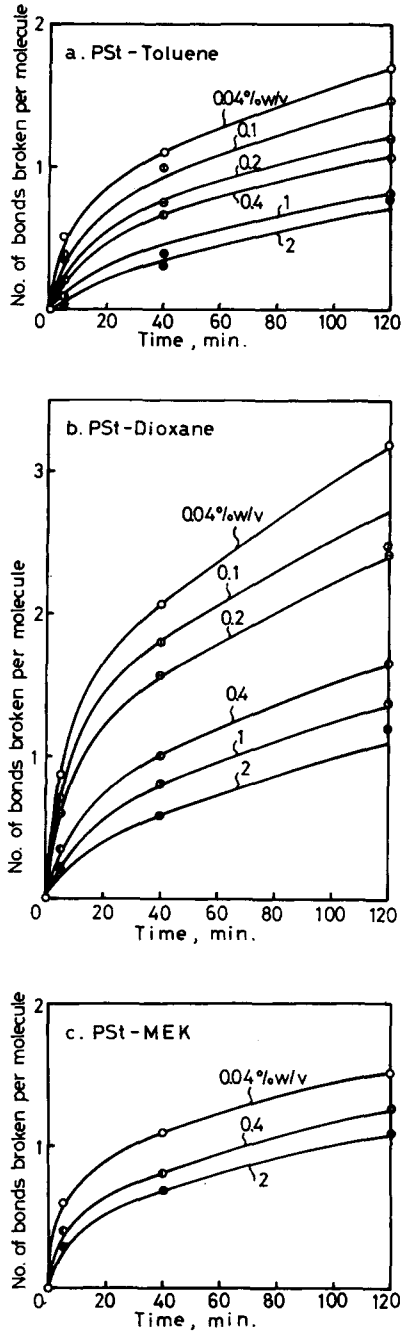


Fig. 4. Relationship between number of scissions per polymer molecule and stirring time for PSt in (a) toluene, (b) dioxane, and (c) methyl ethyl ketone at several concentrations: (●) 2% w/v; (◐) 1%; (◑) 0.4%; (◒) 0.2%; (◓) 0.1%; (○) 0.04%.

This is considered to be caused by insufficient stirring time and different molecular weight distribution of PSt before stirring, such as different content of components below P_1 .

TABLE II
Values of P_1 , P_2 , and k for Poly(methyl Methacrylate) in Several Solvents^a

| Polymer concentration, % w/v | Chloroform | | | Benzene | | | Ethyl acetate | | |
|------------------------------|------------|-------|----------------------------------|---------|-------|----------------------------------|---------------|-------|----------------------------------|
| | P_1 | P_2 | $k \times 10^6, \text{min}^{-1}$ | P_1 | P_2 | $k \times 10^6, \text{min}^{-1}$ | P_1 | P_2 | $k \times 10^6, \text{min}^{-1}$ |
| 2 | 4560 | 3420 | 10 | 4440 | 3330 | 14 | 3500 | 2630 | 13 |
| 1 | 3660 | 2750 | 12 | 3980 | 2990 | 15 | 3500 | 2630 | 13 |
| 0.4 | 2330 | 1750 | 18 | 3420 | 2570 | 16 | 3500 | 2630 | 13 |
| 0.2 | 2110 | 1580 | 20 | 3060 | 2300 | 22 | 3170 | 2380 | 14 |
| 0.04 | 1510 | 1130 | 40 | 1920 | 1440 | 29 | 2580 | 1940 | 21 |

^a At 30,000 rpm, 30°C, $P_0 = 6,200$.

TABLE III
Values of P_1 , P_2 , and k for Polystyrene in Several Solvents^a

| Polymer concentration, % w/v | Toluene | | | Dioxane | | | Methyl ethyl ketone | | |
|------------------------------|---------|-------|----------------------------------|---------|-------|----------------------------------|---------------------|-------|----------------------------------|
| | P_1 | P_2 | $k \times 10^6, \text{min}^{-1}$ | P_1 | P_2 | $k \times 10^6, \text{min}^{-1}$ | P_1 | P_2 | $k \times 10^6, \text{min}^{-1}$ |
| 2 | 3830 | 2870 | 6.3 | 2950 | 2210 | 10.0 | 3460 | 2600 | 11.6 |
| 1 | 3800 | 2850 | 8.7 | 2840 | 2130 | 10.3 | — | — | — |
| 0.4 | 3400 | 2550 | 11.1 | 2570 | 1930 | 12.0 | 3150 | 2360 | 13.0 |
| 0.2 | 3190 | 2390 | 11.6 | 2020 | 1520 | 17.4 | — | — | — |
| 0.1 | 2890 | 2170 | 13.7 | 1860 | 1400 | 19.5 | — | — | — |
| 0.04 | 2620 | 1970 | 14.8 | 1630 | 1220 | 20.1 | 2910 | 2180 | 18.9 |

^a At 30,000 rpm, 30°C, $P_0 = 5,610$.

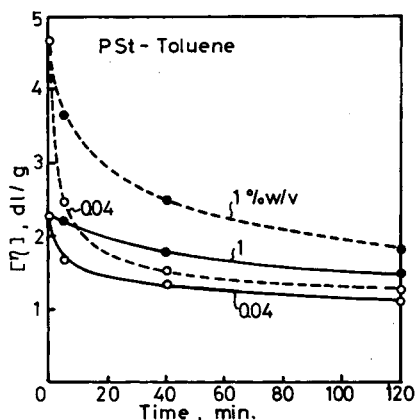


Fig. 5. Degradation of PSt with different initial degree of polymerization: broken curve, $P_0 = 15,300$; solid curve, $P_0 = 5,610$; (●) 1% w/v; (○) 0.04% w/v.

DISCUSSION

Relationship between Total Number of Scissions and Polymer Concentration

Relationships between total number of scissions of polymer in solutions after stirring for 120 min and polymer concentration are shown in Figures 6a and 6b for PMMA and PSt, respectively. It is found that total number of scissions increased with increasing polymer concentration in every solvent, but that it increased in different ways.

For PMMA in ethyl acetate, the total number of scissions increased linear-

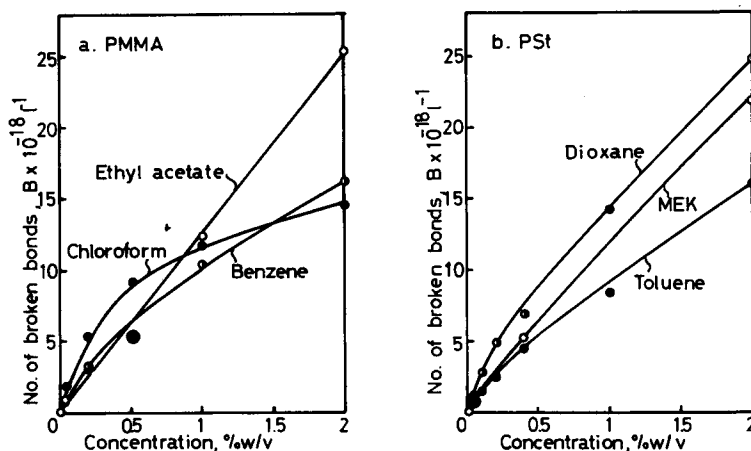


Fig. 6. Relationships between total number of scissions of polymer after 120 min of stirring and polymer concentration for (a) PMMA and (b) PSt in various solvents, at 30,000 rpm, 30°C.

ly in proportion to polymer concentration; but in chloroform it increased linearly over 0.5% w/v. In benzene, an intermediate tendency was found.

For PSt in MEK, the total number of scissions in polymer solution increased relatively linearly in proportion to polymer concentration in the range from low to high concentration, whereas it increased linearly in the range over 0.2% w/v to 0.4% w/v in dioxane and toluene. Although MEK was the best solvent for PSt from the viewpoint of θ -temperature, it gave a low $[\eta]$ at the stirring temperature.

In a solvent giving a high $[\eta]$, increase in concentration did not linearly increase the total number of scissions in polymer solution, and so the line showing the relationship became curved. The deviation from linearity is considered to show that polymer molecules suppressively interacted with each other in the scission reaction or that they decreased the shearing force.

Relationship Between Limiting Degree of Polymerization and Polymer Concentration

Relationships between limiting degree of polymerization P_1 and polymer concentration for PMMA and PSt are plotted in Figures 7a and 7b. It is clearly shown that polymer chains are broken to lower degree of polymerization with decreasing polymer concentration. It seems that P_1 increases with polymer concentration, reaching a certain value intrinsic to the solvent.

The effect of change in PMMA concentration on P_1 is relatively small for the poor solvent ethyl acetate, being quite absent at concentrations over 0.4% w/v. It is large in the good solvent chloroform, but small in the poor solvent ethyl acetate. In benzene, it is medium in effect.

Effect of addition of phenyl- β -naphthylamine was not observed.

For PSt, concentration dependence of P_1 was small in MEK but large in dioxane and toluene. It became smaller at higher concentrations even in the latter two solvents. It is also recognized for PSt from the above results that the concentration dependence of P_1 is large in a solvent giving a high $[\eta]$ and

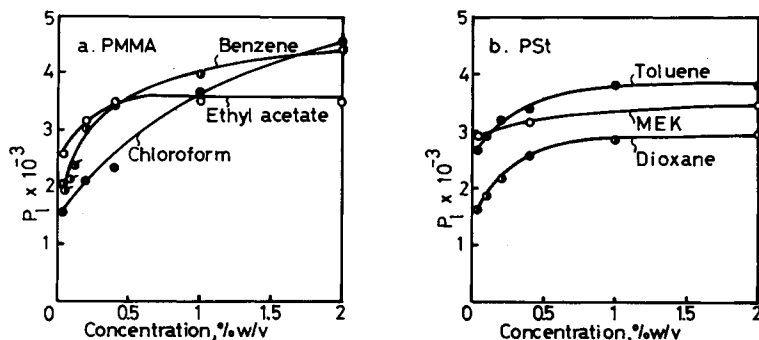


Fig. 7. Effects of polymer concentration on limiting degree of polymerization for (a) PMMA and (b) PSt in various solvents.

small in one giving a low $[\eta]$. It was reported in the previous study³ that the better a solvent was, that is, the wider polymer chains were expanded in the solvent, the higher P_1 was. However, it was found in this study that at a low concentration, such as 0.04% w/v, the better a solvent was, the lower P_1 was, if a solvent giving a higher $[\eta]$ is defined as a better solvent. The conclusion in the previous paper³ should be corrected to be true only in the case of a relatively higher concentration, such as 2% w/v. Different results can be obtained in another lower concentration. The effect of solvent on P_1 was found not to be simple, being involved in the concentration.

The observations that polymer molecules were ruptured to shorter chain lengths in a good solvent (where they were expanded wider and so given larger intrinsic viscosities), and vice versa in a poor one by low-concentration stirring, suggest that polymer molecules are ruptured to a constant hydrodynamic volume regardless of kind of solvent. The products of limiting degree of polymerization and intrinsic viscosity in the solvent used for stirring gave nearly constant values, which are proportional to the hydrodynamic volume according to Flory.¹⁴ The relationship between the final degree of polymerization and the hydrodynamic volume will be discussed elsewhere in detail. In any way, polymer chains are found to be ruptured to a lower degree of polymerization with decreasing concentration in the range between 0.04% and 2% w/v regardless of kind of polymer and solvent.

Relationship Between Rate Constant of Scission and Polymer Concentration

In Figures 8a and 8b are plotted relationships between polymer concentration and rate constant of scission, k , for PMMA and PSt in several solvents, respectively.

The tendency is found that the effect of concentration on k is small, k being nearly constant, in the concentration range over 0.5% or 1% w/v for every solvents but that it is large below the concentration range. Moreover, the tendency becomes more distinguished in the solvent giving a higher $[\eta]$. The conclusion in the previous study^{1,2} that the effect of polymer concentration is small is right only at a relatively high concentration. So it is not inconsistent with the results obtained here.

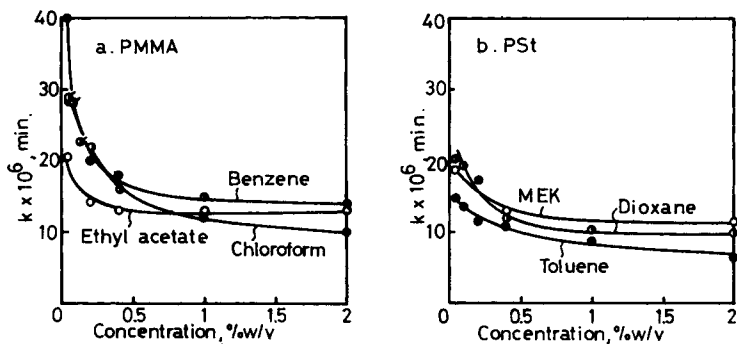


Fig. 8. Effects of polymer concentration on rate constant of scission for (a) PMMA and (b) PSt in various solvents.

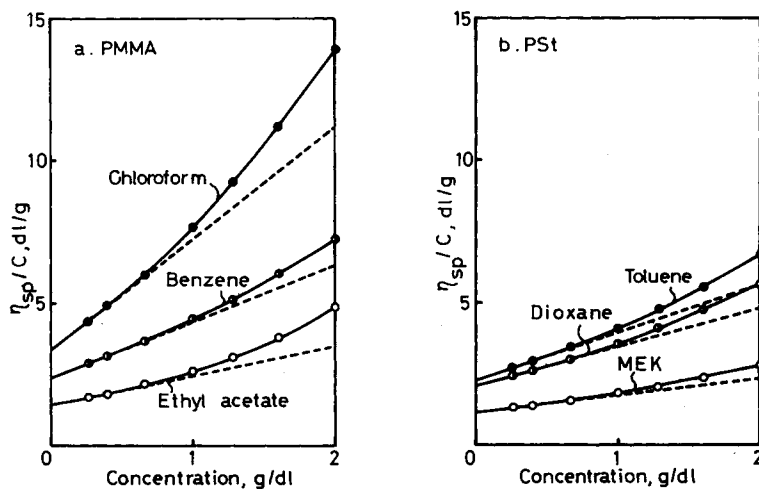


Fig. 9. Relationship between η_{sp}/C and C for (a) PMMA and (b) PSt in various solvents.

Oxidation reaction is generally not negligible at low concentrations. Therefore, the effect of oxidation on scission was investigated as follows. Polymer solutions containing 1% of antioxidant phenyl- β -naphthylamine to the weight of polymer were prepared and stirred. The results are given by the dashed circles, showing the same tendency as obtained without any antioxidant. It is considered that oxidation reaction did not largely affect the scission of chains.

Interaction between polymer molecules is considered to suppress the scission reaction, because for both cases of PMMA and PSt, large values of k were found at the very low concentration where the interaction seemed to be negligible, and small ones were found at the high concentration where some interaction appeared. For the sake of reference, relationship between η_{sp}/C and C (where η_{sp} is specific viscosity and C is concentration) is shown in Figures 9a and 9b. Generally, linearity is absent over concentrations near 0.5–1% w/v for both polymers, the interaction between polymer molecules being significant. The concentration 0.5–1% w/v is considered to have some rela-

tion to the boundary concentration where concentration dependences of P_1 and k appear.

CONCLUSIONS

It was found that concentration had little effect on the chain scission by high-speed stirring over concentrations of 0.5% or 1% w/v, whereas it had a significant effect below the concentration, that is, the limiting degree of polymerization P_1 decreased and the rate constant of scission k increased with decreasing concentration and that the concentration dependence of P_1 and k was large in solvents giving high $[\eta]$ and small in solvents giving low $[\eta]$.

When P_1 -versus- C curves are extrapolated to concentration zero % w/v, P_1 seems to reach certain values over 1000 and k to increase furthermore for every solvent. It remains a question whether k increases infinitely or not. The authors presume that it reaches a constant value below a certain concentration. The results by extrapolation are quite opposite to those obtained by Rodriguez.⁵

It was made clear that concentration dependences of P_1 and k became remarkable below 0.5% w/v, where usually interaction between polymer molecules became small, and moreover, that below that concentration, a decrease in concentration affects favorably the scission of chains.

It is concluded from these observations that a polymer chain in solution is ruptured by high-speed stirring rather more rapidly and more violently in isolated state and that the scission of a polymer chain is suppressed by neighboring polymers by interaction between them or by some unfavorable effect, such as the decrease in the shear rate due to a polymer-solvent-neighboring polymer interaction.

A part of this study was presented at the 26th (in April, 1972 at Kanagawa Pref.) and 30th (in April, 1974 at Osaka Pref.) Annual Meetings of the Japan Chemical Society.

References

1. Y. Minoura, T. Kasuya, S. Kawamura, and A. Nakano, *J. Polym. Sci. A-2*, **5**, 125 (1967).
2. A. Nakano and Y. Minoura, *J. Appl. Polym. Sci.*, **15**, 927 (1971).
3. A. Nakano and Y. Minoura, *J. Appl. Polym. Sci.*, **16**, 627 (1972).
4. F. Bueche, *J. Appl. Polym. Sci.*, **4**, 101 (1960).
5. F. Rodriguez and C. C. Winding, *Ind. Eng. Chem.*, **51**, 1281 (1959).
6. H. Gröhn and G. Opitz, *Plaste Kaut.*, **11**, 11 (1964).
7. W. R. Johnson and C. C. Price, *J. Polym. Sci.*, **45**, 217 (1960).
8. H. Fujiwara and K. Goto, *Kobunshi Kagaku*, **21**, 716 (1964).
9. H. Fujiwara and K. Goto, *Kogyo Kagaku Zasshi*, **71**, 1430 (1968).
10. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1966, p. IV-163; T. G. Fox, Jr., and P. J. Flory, *J. Amer. Chem. Soc.*, **73**, 1915 (1951); L. H. Cragg, E. T. Dumitru, and J. E. Simkins, *J. Amer. Chem. Soc.*, **74**, 1977 (1952); T. G. Fox, Jr., and P. J. Flory, *J. Amer. Chem. Soc.*, **73**, 1909 (1951); *ibid.*, *J. Phys. Colloid Chem.*, **53**, 197 (1949).
11. A. V. Tobolsky, *J. Polym. Sci.*, **9**, 171 (1952).
12. A. V. Tobolsky, *J. Amer. Chem. Soc.*, **74**, 938 (1952).
13. D. W. Ovenall, G. W. Hastings, and P. E. M. Allen, *J. Polym. Sci.*, **33**, 203 (1958).
14. P. J. Flory and T. G. Fox, *J. Amer. Chem. Soc.*, **73**, 1904 (1951).

Received November 15, 1974

Revised January 9, 1975