

Effect of Solvents on the Degradation of Polymers by High-Speed Stirring*

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Synopsis

The effect of solvents on the degradation of poly(methyl methacrylate), polystyrene, and polyisobutylene by high-speed stirring (30,000 rpm) at 30°C was studied. From the intrinsic viscosities of polymers stirred for given times, the viscosity-average degree of polymerization, \bar{P}_v , was obtained and the number of scissions per molecule, B/n_0 , was calculated. Ovenall's equation

$$dB_i/dt = k(P_i - P_i)n_i$$

could be applied to the results, where dB_i/dt is the rate of breakage of molecules of i th degree of polymerization, n_i is the number of molecules present, P_i is the limiting degree of polymerization, and k_i is a rate constant; k and P_i were changed with solvents, and were found to have no relation to the physical properties of the solvents but to the intrinsic viscosities the polymers showed in the solvents used for the stirring. k was smaller and P_i larger for solvents where polymers had larger intrinsic viscosities. This relation implies that the degree of expansion of a polymer coil in a solvent is closely related to the rate constant of scission and to the limiting degree of polymerization.

INTRODUCTION

When polymer solutions are stirred at high speed or irradiated with ultrasonic waves, the intrinsic viscosities of the recovered polymers are decreased. The decrease in intrinsic viscosity is caused by scission of the polymer chains.

The mechanism of scission, however, has not been made clear. Schmid and Rommel¹ considered that the breaking of polymer by ultrasonic irradiation was brought about by the friction between solvent and polymer molecules. On the other hand, it has been claimed by some²⁻⁴ that cavitation was essential to the scission of polymer chains. Other investigators^{1,5} showed that cavitation was not always necessary for scission. It was considered that the force of friction between solvent and polymer chain was an effective cause of scission.

However, the role of interaction between polymer molecules in solution in the rupture of the molecules remained uncertain. Our previous study^{6,7} and

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the present work were carried out to clarify this role. It has been established² that scission of polymer molecules by high-speed stirring in 1-4% solutions was not caused by intermolecular interactions, although entanglement was thought to be present in the concentration range tested. Entanglement and collision between polymer molecules due to cavitation or turbulent flow were not predominantly responsible for scission of polymers. Rather, rate and limit of scission of polymer molecules were dependent on the solvents.

Many papers on the effect of solvents have already been presented and interesting results were obtained.^{6,8-14} Nevertheless, it is not yet clear how the change in solvent affects the rate and limit of degradation. The effect of solvents on scission of polymer chains has scarcely been discussed quantitatively. In order to solve the problem, the physical properties relating to cavitation and some parameters indicating the interaction between solvent and polymer must be taken up, and the relation between them and the rate or limit of degradation must be discussed quantitatively. In this paper, the results of experiments carried out on the above premise are reported.

EXPERIMENTAL

Materials

Poly(methyl Methacrylate). The same poly(methyl methacrylate) (PMMA) as that in the previous paper⁷ was used. Intrinsic viscosity in benzene at 30°C was 2.80 dl/g. Molecular weight was 705,000; degree of polymerization $\bar{P}_n = 7,050$.

Polystyrene. Polystyrene (PSt) spontaneously polymerized in the dark was used. The polymer was dissolved in benzene, precipitated in methanol, filtered, and dried for purification. Intrinsic viscosity in benzene at 30°C was 3.80 dl/g. Molecular weight was 1,200,000; degree of polymerization $\bar{P}_n = 11,500$.

Polyisobutylene. Polyisobutylene, Vistanex MML-100 (PIB) made by Esso Standard Petroleum Co. was used as is. Intrinsic viscosity in benzene at 30°C was 1.34 dl/g. Molecular weight was 927,000, degree of polymerization $\bar{P}_n = 16,500$.

Solvents. Solvents used for stirring were acetonitrile, ethyl acetate, toluene, methyl methacrylate, acetone, chloroform, benzene, and 1,2-dichloroethane for PMMA; cyclohexane, toluene, methyl ethyl ketone, and dioxane for PSt; and benzene, toluene, *n*-hexane, carbon tetrachloride, and cyclohexane for PIB. They were purified by the usual methods.

Methods

Apparatus for Stirring. A. T. K. Homomixer of HS-M type made by Tokushu Kika Kogyo Co., Ltd., was used as high-speed stirrer. The stator, turbine, and vessel of the mixer were the same as those used in the previous experiment.⁶

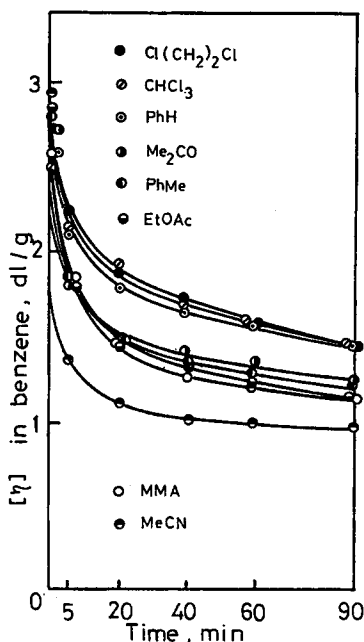


Fig. 1. Degradation of poly(methyl methacrylate) by high-speed stirring (30,000 rpm) in various solvents at 20°C: polymer concentration, 2% w/v; (●) 1,2-dichloroethane; (⊙) chloroform; (○) benzene; (⊙) acetone; (●) toluene; (⊖) ethyl acetate; (○) methyl methacrylate; (●) acetonitrile.

Method of Stirring. Solutions containing 4 g polymer in 200 ml solvent (this concentration is abbreviated as 2% w/v hereafter) were stirred. Other experimental conditions were the same as in the previous paper.⁷ Speed was 30,000 rpm, and temperature of solutions was maintained at $30 \pm 5^\circ\text{C}$.

Method of Separation. The solutions stirred for given times were removed from the apparatus and dried by hot air until no decrease in the weight of dried polymer occurred. The intrinsic viscosity of the polymer thus separated was beforehand compared with that determined by the reprecipitation method. No difference was found between the two methods.

Measurement of Intrinsic Viscosity. Intrinsic viscosities of polymers for the calculation of the degree of degradation were all measured in benzene at $30 \pm 0.05^\circ\text{C}$ using an Ubbelohde viscometer. The equations used for the calculation of viscosity-average degree of polymerization, \bar{P}_v , or molecular weight, \bar{M}_v , are as follows:

$$\bar{P}_v = 2200 [\eta]^{1.13} \quad \text{for PMMA}^{15}$$

$$\bar{P}_v = 1770 [\eta]^{1.40} \quad \text{for PSt}^{16}$$

$$[\eta] = 6.1 \times 10^{-4} \bar{M}_v^{0.56} \quad \text{for PIB}^{17}$$

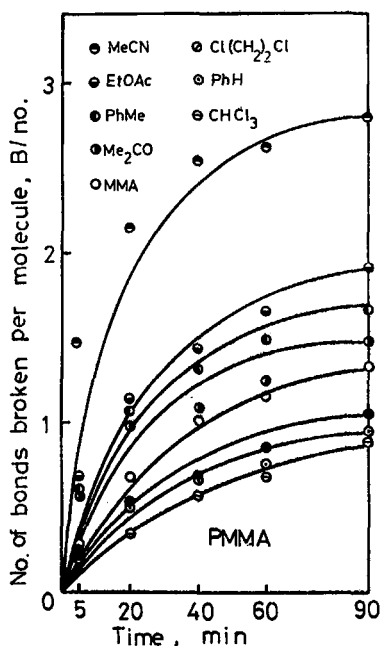


Fig. 2. Number of bonds broken per polymer molecule during high-speed stirring (30,000 rpm) of poly(methyl methacrylate) in various solvents at 20°C: polymer concentration, 2% w/v; (●) acetonitrile; (◐) ethyl acetate; (◑) toluene; (◒) acetone; (○) methyl methacrylate; (◓) 1,2-dichloroethane; (◔) benzene; (◕) chloroform.

Intrinsic viscosities of three kinds of polymers for the parameter indicating interaction between polymers and solvents were measured for different polymer-solvent systems at $30 \pm 0.05^\circ\text{C}$, except for the polystyrene-cyclohexane system, which was measured at $35 \pm 0.05^\circ\text{C}$. (At 30°C , polystyrene is insoluble in cyclohexane.) Poly(methyl methacrylate), polystyrene, and polyisobutylene with constant degrees of polymerization of 7,050, 12,400, and 15,200, respectively, were used for the measurements.

RESULTS

Stirring of Poly(methyl Methacrylate) Solution

The decrease in intrinsic viscosity of PMMA in various solvents with high-speed stirring is shown in Figure 1. Concentration increased somewhat during stirring, but its effect on the degradation was negligible.⁷ The $[\eta]$ value decreased rapidly at first and then slowly, reaching a constant value depending on the solvent. A similar tendency was also observed for stirring in mixed solvents which are not shown in the figure. The number of scissions was calculated by using the equation

$$B/n_0 = \bar{P}_0/\bar{P}_t - 1$$

TABLE I
Results and Related Values for Poly(methyl Methacrylate)

Solvents	Results ^a				Values depending on solvent and polymer		
	P_0	P_t	P_∞	$k \times 10^6$, min ⁻¹	θ temp., °C	Viscosity of so- lution, ^b cp	$[\eta]$, ^c dl/g
Acetonitrile	8120	2840	2130	32	30 or 45	1.13	0.45
Ethyl acetate	7810	3440	2580	18	-98	5.38	1.56
Toluene	7700	3750	2810	19	-65	4.82	1.84
Methyl methacrylate	6150	3360	2520	16	-163 ± 50	—	1.96
Acetone	7400	4000	3000	20	-55	2.47	1.56
Acetone 75, chloro- form 25	6370	3780	2830	16	—	—	2.32
Acetone 50, chloro- form 50	6740	3800	2850	16	—	—	2.66
Acetone 25, chloro- form 75	6320	3930	2950	12	—	—	3.19
Chloroform	6670	4400	3300	11	—	—	3.19
Chloroform	6760	4500	3380	10	-273 ± 50	13.20	3.50
Benzene	6980	4650	3500	14	-223 ± 50	5.58	2.80
1,2-Dichloroethane	7430	4660	3500	13	-233 ± 50	13.75	2.92

^a Values in Ovenall's equation agree with results. So do the values in Tables II, III, and IV.

^b Values of solutions containing 2.0 g polymer in 100 ml solvents at 30°C.

^c Values at 30°C shown by the polymer of constant degree of polymerization in the solvents used for stirring.

where \bar{P}_0 and \bar{P}_t are the degree of polymerization before and after stirring for time t , respectively.

It is more accurate to use the number-average degree of polymerization, \bar{P}_n , to calculate the number of scissions, since the D.P. distribution varies with the scission of polymer chains. However, \bar{P} , was used here for convenience.

The relationship between stirring time and number of scissions is shown in Figure 2. The rate of scission is large at first, and then small. Rate constant of scission, k , and the limiting degree of polymerization, P , in Ovenall's equation (2) were determined by the trial-and-error method previously described.¹⁰ Theoretical curves obtained using k and P thus determined are shown in Figure 2; k , P_t , initial degree of polymerization P_0 (D.P. of original polymer), and final degree of polymerization P_∞ (D.P. obtained after stirring for infinite time) for each solvent are listed in Table I.

Ovenall's rate equation¹⁸

$$\left. \begin{aligned} \frac{dB_t}{dt} &= k(P_t - P_t)n_t & (P_t > P_t) \\ \frac{dB_t}{dt} &= 0 & (P_t \leq P_t) \end{aligned} \right\} \quad (1)$$

where dB_i/dt is the rate of breakage of molecules of degree of polymerization P_i , n_i is the number of such molecules, k is a rate constant, and P_i is the limiting D.P. below which molecules cannot be degraded.

Integrating eq. (1) yields

$$\frac{B}{n_0} = \left[\frac{4}{3} \cdot \frac{P_0}{P_i} - 1 \right] - \left[\frac{1}{3} \cdot \frac{P_0}{P_i} - \frac{1}{2} \right] \exp \left(-\frac{3}{2} k P_i t \right) - \left[\frac{P_0}{P_i} - \frac{1}{2} \right] \exp \left(-\frac{1}{2} P_i k t \right) \quad (2)$$

where B is the number of bonds broken in a system after stirring for time t , n_0 is the number of molecules before stirring, and P_0 is the D.P. before stirring.

Stirring of Polystyrene Solution

The increase in number of scissions per polymer chain for the degradation of PSt in various solvents is shown as a function of stirring time by circles in Figure 3. Theoretical curves calculated by Ovenall's equation using appropriate values of k and P_i are shown by solid lines. Related values are listed in Table II.

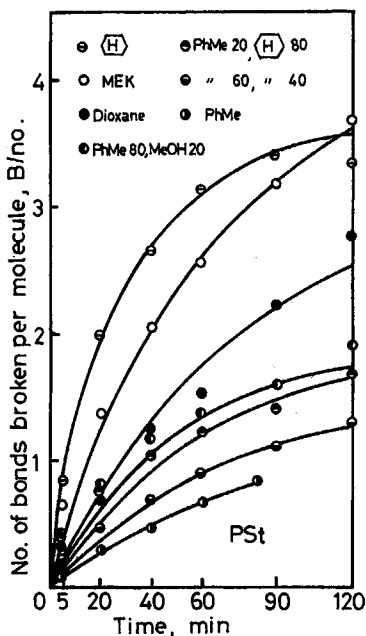


Fig. 3. Number of bonds broken per polymer molecule during high-speed stirring (30,000 rpm) of polystyrene in various solvents at 20°C: polymer concentration, 2% w/v; (H) cyclohexane; (O) methyl ethyl ketone; (●) dioxane; (●) toluene 80, methanol 20; (●) toluene 20, cyclohexane 80; (●) toluene 60, cyclohexane 40; (●) toluene.

TABLE II
Results and Related Values for Polystyrene^a

Solvents	Results				Values depending on solvent and polymer		
	P_0	P_t	P_∞	$k \times 10^6$, min ⁻¹	θ temp., °C	Viscosity of solu- tion, cp	$[\eta]$, dl/g
Cyclohexane	7000	2940	2200	12	34	3.10	0.71
		7000	2200	12			
Cyclohexane 80, toluene 20	8180	3640	2730	8	—	—	1.34
Cyclohexane 60, toluene 40	6820	3240	2430	7	—	—	2.00
Cyclohexane 40, toluene 60	8750	4400	3300	6	—	—	2.30
Cyclohexane 20, toluene 80	8300	4800	3600	5.5	—	—	2.40
Toluene	8200	4200	3150	6	-113	7.84	2.30
		12200	8000	6000			
Toluene 93, methanol 7	11100	4800	3600	4	—	—	2.33
Toluene 86, methanol 14	11600	6000	4500	6	—	—	2.02
Toluene 80, methanol 20	9900	4400	3300	8	—	—	1.44
Methyl ethyl ketone	11300	2560	1920	7.7	-273	2.41	1.20
Dioxane	11400	3340	2500	5.5	-75	13.65	2.22

^a See footnotes in Table I.

TABLE III
Results and Related Values for Polyisobutylene^a

Solvents	Results				Values depending on solvent and polymer		
	P_0	P_t	P_∞	$k \times 10^6$ min ⁻¹	θ temp., °C	Viscosity of solu- tion, cp	$[\eta]$, dl/g
Benzene	16500	3470	2600	7.5	24	5.08	1.28
Toluene	16500	4000	3000	6.0	12	7.84	2.20
<i>n</i> -Hexane	17600	4800	3600	5.8	-273	5.56	2.60
Carbon tetrachloride	15000	3600	2700	3.7	—	24.80	3.70
Cyclohexane	17000	4100	3080	3.2	-147	27.75	4.10

^a See footnotes in Table I.

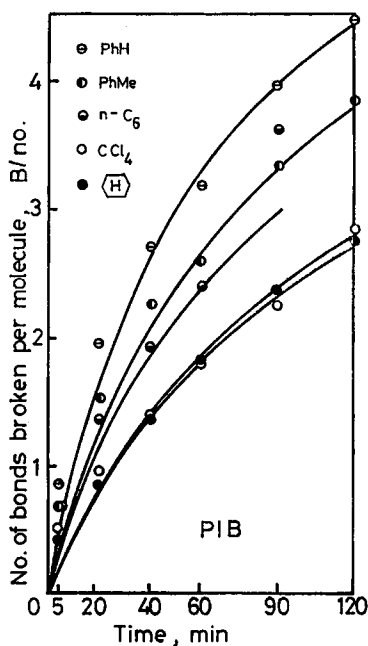


Fig. 4. Number of bonds broken per polymer molecule during high-speed stirring (30,000 rpm) of polyisobutylene in various solvents at 20°C: polymer concentration, 2%w/v; (⊖) benzene; (●) toluene; (⊖) *n*-hexane; (○) carbon tetrachloride; (●) cyclohexane.

TABLE IV
Results and Related Values for Poly(ethylene Oxide)^a

Solvents	Results ^b				Values depending on solvent and polymer		
	P_0	P_t	P_∞	$k \times 10^6$ min ⁻¹	θ temp., °C	Viscosity of so- lution, cp	$[\eta]$, dl/g
Carbon tetrachloride	17500	935	700	30	—	15.29 ^c	0.29 ^c
Ethyl benzene	23600	4540	3400	12	—	4.20 ^e	0.98 ^e
Ethyl acetate	18200	3870	2900	13	—	10.95 ^c	2.87 ^c
Acetonitrile	17100	2120	1590	28	—	8.01 ^c	3.17 ^c
Toluene	25500	5340	4000	8	—	21.31 ^e	3.63 ^e
Benzene	19200	6940	5200	7	—	37.52 ^d	5.00 ^d
Water	22700	9080	6800	6	—	—	5.30 ^d
1,2-Dichloroethane	18200	4250	3180	9	—	72.20 ^e	6.35 ^c

^a See footnotes in Table I.

^b Calculated from the results reported by Minoura et al.⁶

^c Values at 30°C.

^d Values at 35°C.

^e Values at 40°C.

The effect on degradation of standing time after preparation of a solution was investigated for the solution containing 4 g polystyrene in 142.8 ml dioxane and 57.2 ml methanol. Solutions immediately after and 65 hr after preparation were stirred at a speed of 30,000 rpm, and the decrease in $[\eta]$ was compared. But a difference in $[\eta]$ of more than 0.08 dl/g for the same stirring time was not found, and curves of decrease in $[\eta]$ are superposed. Standing time after preparation of solutions was found not to affect the degradation.

Stirring of Polyisobutylene Solution

Increase in the number of scissions with stirring time for the degradation of PIB in various solvents is shown by circles in Figure 4. Theoretical curves are shown by solid lines in the figure. Related values are listed in Table III.

Table IV lists k , P_i , etc., in Ovenall's equation calculated from the results⁶ with poly(ethylene oxide).

DISCUSSION

Relationship Between Rate Constant of Scission and Various Properties of Solvents

Various physical properties of solvents which are considered to be related to scission of polymer chains are listed in Table V. It was supposed that the vapor pressure of a solvent in a cavity was high for a low-boiling-point solvent when cavities were formed by cavitation, and vice versa. The pressure might affect the violence of collision of a liquid at the collapse of the cavity to relate to the rate constant of scission.

The relationship between boiling point of solvent and the constants relating to scission obtained for the solvent was investigated. Heat of evaporation was also contrasted with the constants from the same viewpoint, but these properties did not appreciably affect the scission.

The viscosities of the solvents itself were not directly correlated to the rate constant of scission. Density, molecular weight, and molar volume are factors which might be involved in the collision between solvent and polymer molecules, but no relation was found.

Solubility parameter (S.P.) is a good index for judging whether a solvent is good or poor for a polymer. It had no direct relation to the rate constant.

Relationship Between Rate Constant of Scission and Viscosity of a Solution

Viscosity of a solution depends upon the viscosity of the solvent itself, the size of polymer molecules, and the magnitude of the interaction between them. At higher concentration, over 1% w/v, this magnitude must be

TABLE V
 Properties of Solvents

Solvents	Molecular weight	Density, g/cm ³	Molar volume, cm ³ /g	Boiling point, °C	Heat of evaporation, kcal/mole	Solubility parameter (S.P.) ^a	Viscosity at 30°C, cp
Acetonitrile	41.1	0.78 (25°C)	52.7	81.6	7.1	11.9	0.325
Ethyl acetate	88.1	0.89 (25°C)	99.0	77.1	7.7	9.0	0.637
Toluene	92.1	0.86 (25°C)	107.1	110.6	9.1	8.9	0.522
Methyl methacrylate	100.1	0.94 (20°C)	106.5	100.3	—	—	—
Acetone	58.1	0.78	74.5	56	7.1	9.8	0.293
Chloroform	119.4	1.49 (20°C)	80.1	61.2	7.0	9.2	0.514
Benzene	78.1	0.87 (25°C)	89.1	80.1	8.1	9.2	0.56
1,2-Dichloroethane	98.9	1.24 (30°C)	79.8	83.4	7.7	9.8	0.73
Cyclohexane	84.0	0.78	107.7	80.7	7.89	8.2	0.82
Methyl ethyl ketone	72.1	0.80 (25°C)	90.1	79.5	7.6	7.3	0.365
Dioxane	88.1	1.02 (25°C)	86.4	101	8.55	10.0	1.06
n-Hexane	86.1	0.66	130.5	68.7	7.54	7.3	0.29
Carbon tetrachloride	153.8	1.58 (25°C)	97.3	76.8	7.16	8.6	0.84
Ethyl benzene	106.1	0.86 (25°C)	123.3	136.2	10.1	8.7	0.59
Water	18.0	1.00	18.0	100.0	10.51	23.4	0.80

^a Calculated²⁴ solubility parameter (S.P.) values for poly(methyl methacrylate), polystyrene, polyisobutylene, and poly(ethylene oxide) are 9.25 (9.0-9.5), 9.12 (9.1), 7.7 (8.05) and 8.6 (-), respectively; values in parentheses are observed values.

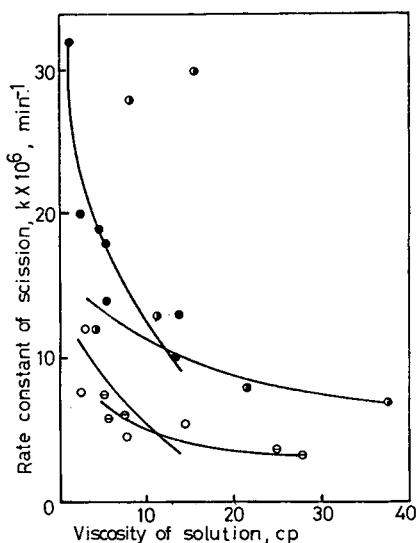


Fig. 5. Relationship between rate constant of scission and viscosity of solution for each polymer: (●) poly(methyl methacrylate) (PMMA); (●) poly(ethylene oxide) (PEO); (○) polystyrene (PSt); (⊖) polyisobutylene (PIB). (Viscosities were measured for solution containing 2 g polymer in 100 ml solvent.)

large enough not to be negligible. Therefore it is unreasonable to compare the viscosity of a solution uniformly. But viscosities of solutions containing 2.0 g nondegraded polymers in 100 ml solvents were measured and relationship between them and the rate constants of scission was investigated. The relationships are shown in Figure 5. Though it is not striking, a tendency is found for rate constants of scission to be small for viscous solutions. As a good solvent makes a more viscous solution for the same concentration, the tendency suggests, as was pointed out before,¹⁹ that there is a certain relationship between quality of solvent and rate constant.

Relationship Between Rate Constant of Scission and θ Temperature

It was the consensus in many papers that the mechanical scission of polymers in solution depended on the solvents and that polymer chains were more easily ruptured in a poor solvent than in a good one. The θ temperature²⁰ for each system as an index whether each solvent is good or poor is listed in Tables I-IV. The systems whose θ temperatures were measured were not numerous. The degree of expansion of polymers is identical and the second virial coefficient is zero at θ temperature regardless of change in solvent. But the degree of expansion is different for each solution at the stirring temperature (ca. 30°C) as the difference between θ temperature and the stirring temperature is changed with solvents. It is assumed qualitatively that the temperature difference is a measure of the degree of expansion of a polymer coil. As the stirring temperature was nearly constant (ca. 30°C) in the study, the rate constant of scission k was plotted

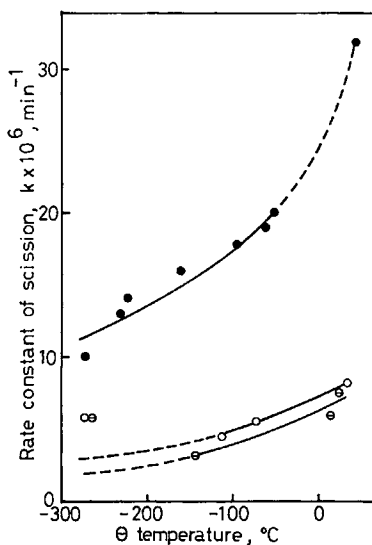


Fig. 6. Relationship between rate constant of scission and temperature for each polymer in various solvents: (●) poly(methyl methacrylate) (PMMA); (○) polystyrene (PSt); (⊙) polyisobutylene (PIB).

against the θ temperature in Figure 6. For poly(methyl methacrylate), a fairly good correlation can be found between them, as shown in Figure 6. Plots are scattered for polystyrene and polyisobutylene, but a similar correlation can be found, except for points for PSt in methyl ethyl ketone and for PIB in *n*-hexane, where θ temperature is -273°C . k was smaller in good solvents of low θ temperature and became larger in solvents of higher θ temperature.

Relationship between Rate Constant of Scission and Intrinsic Viscosity

Relationships between the rate constant of scission k and intrinsic viscosity $[\eta]$ in solvents used for stirring were investigated. The $[\eta]$ values of polymers in solvents at 30°C are listed in the tables. Relationships for poly(methyl methacrylate), polystyrene, and polyisobutylene are shown in Figure 7, 8, and 9, respectively. A negative linear relationship is found between k and $[\eta]$ for all polymers. Almost all points are on a line or near a line for each polymer. P_t tends to increase with increase in $[\eta]$. On the other hand, k and $[\eta]$ were plotted on log-log scales in order to grasp the relation mathematically; they are shown in Figure 10. In Figure 10, slopes of lines are negative and nonlinear. Hence it is considered that k and $[\eta]$ are interrelated in the equation

$$k = k_0 - A[\eta]$$

where k_0 and A are constants depending on kind of polymer, degree of polymerization used for the measurement of intrinsic viscosity, stirring

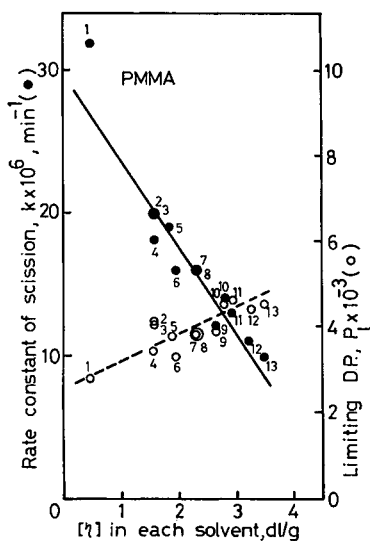


Fig. 7. Relationship between $[\eta]$ of poly(methyl methacrylate) ($\bar{P}_v = 7,050$) in each solvent and rate constant of scission k , (●), and limiting degree of polymerization \bar{P}_i , (○): (1) acetonitrile; (2) and (3) acetone; (4) ethyl acetate; (5) toluene; (6) methyl methacrylate; (7) and (8) acetone 75, chloroform 25; (9) acetone 50, chloroform 50; (10) benzene; (11) 1,2-dichloroethane; (12) acetone 25, chloroform 75; (13) chloroform.

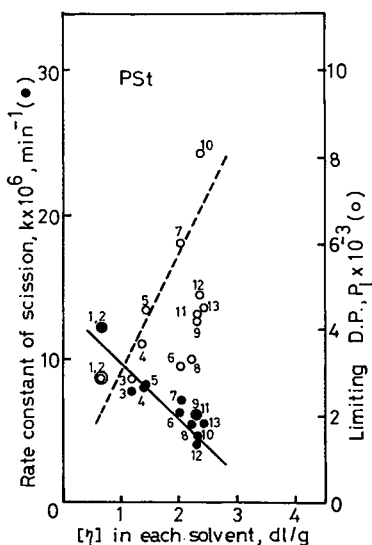


Fig. 8. Relationship between $[\eta]$ of polystyrene ($\bar{P}_v = 12,400$) in each solvent and rate constant of scission k , (●), and limiting degree of polymerization \bar{P}_i , (○): (1) and (2) cyclohexane; (3) methyl ethyl ketone; (4) cyclohexane 80, toluene 20; (5) toluene 80, methanol 20; (6) cyclohexane 60, toluene 40; (7) toluene 86, methanol 14; (8) dioxane; (9) and (10) toluene; (11) cyclohexane 40, toluene 60; (12) toluene 93, methanol 7; (13) cyclohexane 20, toluene 80.

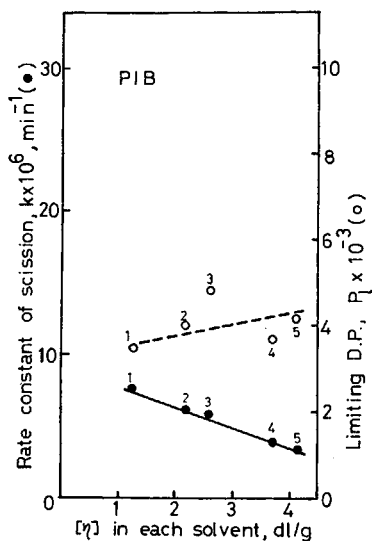


Fig. 9. Relationship between $[\eta]$ of polyisobutylene ($\bar{P}_v = 15,200$) in each solvent and rate constant of scission k , (●), and limiting degree of polymerization P_n , (○): (1) benzene; (2) toluene; (3) *n*-hexane; (4) carbon tetrachloride; (5) cyclohexane.

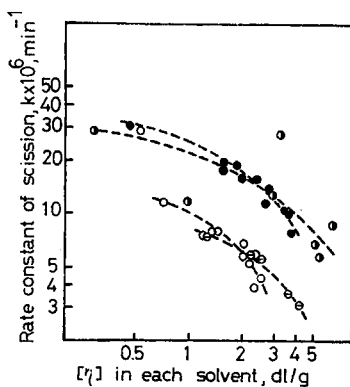


Fig. 10. Relationship between intrinsic viscosities of each polymer in various solvents and rate constant of scission for respective solvent: (●) poly(methyl methacrylate) ($\bar{P}_v = 7,050$); (○) polystyrene ($\bar{P}_v = 12,400$); (⊖) polyisobutylene ($\bar{P}_v = 15,200$); (●) poly(ethylene oxide) ($\bar{P}_v = 19,200$).

speed, and so on, rather than $k = \alpha/[\eta]^\beta$, where α and β are constants. Equations for each polymer are as follows:

$$k = 30.0 \times 10^{-6} - 6.2 \times 10^{-6} \times [\eta] \quad \text{for poly(methyl methacrylate)} \\ (\bar{P} = 7,050)$$

$$k = 14.0 \times 10^{-6} - 4.0 \times 10^{-6} \times [\eta] \quad \text{for polystyrene } (\bar{P} = 12,400)$$

$$k = 9.0 \times 10^{-6} - 1.4 \times 10^{-6} \times [\eta] \quad \text{for polyisobutylene } (\bar{P} = 15,200)$$

As the value of $[\eta]$ decreases, the rate constant of scission increases, not infinitely, but to a constant value. It is found that the rate constant of scission for a polymer-solvent system is closely related to the $[\eta]$ of the polymer in the solvent, as shown above. Since the D.P. of the polymers used for the measurement of $[\eta]$ were different from each other, the dependency of k_0 and A on the kind of polymer cannot be discussed here. If the relationship between k and $[\eta]$ for many kinds of polymers are obtained, a further discussion is perhaps possible. In the previous paper,⁶ the relationship between the $[\eta]$ and the rate constant in Jellinek's equation for poly(ethylene oxide) (PEO) was presented. For comparison with the results in this study on the same basis, P_0 , P_t , P_∞ , and k in Ovenall's equation for PEO were calculated. They are shown in Table IV. The relationship between $\log k$ and $\log [\eta]$ for PEO is shown in Figure 10. It is clear that the rate constant of scission depends upon $[\eta]$, although some scattering is observed.

The solvent where a large $[\eta]$ is measured is a good solvent, and polymer chains are expanded more widely in such a solvent than in a poor solvent. As polymer chains are expanded, the rate constant of scission becomes small, and vice versa. In the concentration range employed in the experiment, the interaction such as entanglement between a polymer chain and an adjacent polymer chain is quite pronounced. If the rupture of a polymer chain depended on this interaction, then the rate constant of scission would be large as the polymer chain is expanded, because the interaction increases with increase in the degree of expansion. However, reverse results were obtained. Therefore the results are considered to show that interaction between a polymer chain and an adjacent chain is not associated with the rupturing process. This is in agreement with the conclusions in the previous paper.¹⁴ As discussed there in detail, the increase in concentration did not promote the degradation of polymer chains. The degradation of polymers was generally decreased rather than promoted with increasing concentration under conditions where a constant energy was applied.^{19, 21-23} Increase in interaction such as entanglement does not always affect favorably scission of polymer chains. We are, of course, convinced of the existence of interaction between polymer molecules at a static or dynamic state; but we also consider that the magnitude of the interaction force is negligible when compared with that of shearing force.

As discussed above, the rate of scission of polymer chains produced by high-speed stirring was rather larger in θ solvents than in others, interaction in such solvents showing less effect on scission. On the other hand, entanglement of polymer chains is considered to be very important for mechanical degradation.

In our opinion, the question of the effect of interaction such as entanglement and contact on scission of polymer chains by mechanical forces remains open, although interaction does exist. Therefore it is desirable to develop the discussion on the question whether entanglement plays an important role or not.

It is considered that the change in solvent directly affected the mechanical degradation of polymer chains through changing the degree of expansion of the polymer chains. Several reasons are considered for the dependency of rate of scission on the degree of expansion of polymer chains. Secondary bonding or geometric interaction between segments of a polymer chain varies with change in the degree of expansion of polymer chains. The number of folds of the chains also changes. As polymer chains are expanded, interaction between segments of each polymer chain becomes small, and vice versa. As shown in Figure 11, the number of folds decrease with a larger degree of expansion, that is, with increase in diameter of the randomly coiled chains for the same chain length. When chains are contracted, the number of folds increases.

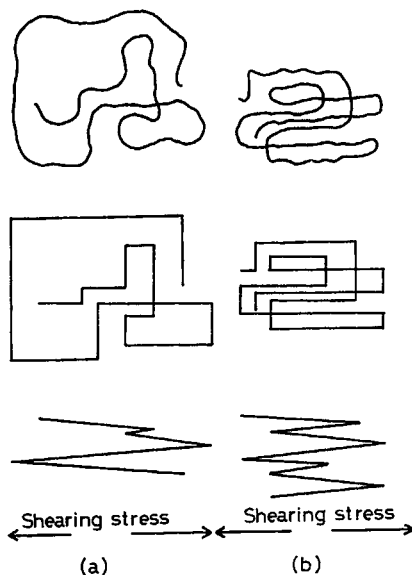


Fig. 11. Randomly coiled models of polymer chains of the same chain length: (a) expanded model; (b) contracted model.

Shear force by high-speed stirring is considered more effective to a contracted polymer chain or a more folded chain than to an expanded one, increasing the rate constant of scission.

The tendency for a larger limiting D.P., P_l , to be obtained for an expanded chain seems to show that P_l also depends on the interaction and the number of folds. P_l is the smallest D.P. below which the shear force required to break a chain does not act. It was found that the scission of polymer chains in solution by high-speed stirring depended mainly on the degree of expansion of the chain and little on the interaction between polymer chains (for example, such as entanglement and collision), in spite of the presence of the interaction over the concentration range used in this experiment. It was also observed that scission of chains hardly took place

when the chains were expanded, but scission proceeded easily when the chains were contracted.

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