

## Degradation of Polymers by High-Speed Stirring\*

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### Synopsis

Benzene solutions containing either poly(ethylene oxide) or poly(methyl methacrylate) or both of varying concentrations were prepared, stirred at a speed of 30,000 rpm, and the effects of concentrations of the same species or different species of polymers on the degradation of the polymers were investigated. Within experimental error little difference was observed in the  $[\eta]$  curves measured for each degraded polymer in spite of change in concentration. It is clear that the degradation of polymer with high-speed stirring in the concentration range 1-4% w/v is not caused by the interaction of polymer chains.

### INTRODUCTION

It is well known that a polymer chain is broken down and that the intrinsic viscosity is decreased when polymer is dissolved in a solvent and stirred at high speed. The polymer chain scission was confirmed by the decrease in intrinsic viscosity of the polymer<sup>1</sup> or by the formation of free radicals.<sup>2</sup>

We have degraded poly(ethylene oxide) by high-speed stirring<sup>3,4</sup> and have shown that the rate of scission with high-speed stirring was comparatively well expressed by Ovenall's<sup>5</sup> eq. (1) or by Jellinek's<sup>6</sup> eq. (2):

$$\frac{dB_i}{dt} = Kn_i(P_i - P_i) \quad (1)$$

$$\frac{dB_i}{dt} = Kn_i(P_i - 1) \quad (2)$$

The effects of polymer concentration, solvent, stirring speed, and initial degree of polymerization on the rate of scission were also investigated.

Goto and Fujiwara<sup>7,8</sup> discussed various experimental data on the mechanical degradation obtained under miscellaneous conditions by various

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methods and found that most results could be well expressed by the following empirical equation:

$$-\frac{dP}{dt} = K(P - P_{\infty})^2 \quad (3)$$

They considered that chain scission was related to the chain length of adjacent polymer molecules, because the rate equation was not expressed by first order of degree of polymerization. It is an interesting question whether intermolecular interaction, intramolecular interaction, or interaction between a polymer molecule and solvent causes the mechanical scission of a polymer molecule. Bueche<sup>9</sup> presented a theory that the entanglements along the chains played a major part in the rupture process for the shear degradation of high polymers. Grohn and Opitz<sup>10</sup> found that the concentration of solution affected the degradation of poly(methyl methacrylate) with high-speed stirring. These reports in a sense recognize an interaction between polymer molecules.

According to our experiments and those of Arai and co-workers,<sup>11</sup> however, the concentration of solution does not affect the rate of mechanical scission of the polymer. A limiting low molecular weight is generally observed in mechanical degradation. These results deny an intermolecular effect.

We have investigated the effect of concentration of the same and different species of polymer using poly(ethylene oxide) and poly(methyl methacrylate) in order to elucidate the mechanism of polymer scission with high-speed stirring.

## EXPERIMENTAL

### Material

**Poly(ethylene Oxide).** Poly(ethylene oxide), PEO-5N, supplied by Seitetsu Kagaku Co., Ltd., was used. Intrinsic viscosity in benzene at 30°C was 3.17. Molecular weight, calculated<sup>3</sup> from the equation  $[\eta] = 6.14 \times 10^{-4} M^{0.64}$  was 640,000 (degree of polymerization 14,500).

**Poly(methyl Methacrylate).** Commercially available methyl methacrylate was washed with aqueous alkali solution to remove inhibitors of polymerization and distilled with water steam. Water of the lower phase was separated. The monomer was dried on sodium sulfate in a cool and dark place, but eventually it polymerized spontaneously. The polymer thus obtained was dissolved in benzene, precipitated with excess methanol, and dried. Poly(methyl methacrylate) thus purified showed an intrinsic viscosity of 2.80 in benzene at 30°C. Molecular weight calculated<sup>12</sup> from the relation equation  $P_n = 2,200[\eta]^{1.13}$  was 770,000 (degree of polymerization 7,700).

**Solvent.** Benzene was used as solvent. Commercially available benzene was purified by the usual method. Poly(ethylene oxide) and poly-

(methyl methacrylate) are not only both soluble in benzene but both are also soluble in benzene without phase separation in the concentration range of the experiment (up to 4% w/v).

### **Stirring Apparatus**

A T. K. Homomixer of HS-M-type made by Tokushu Kika Kogyo Co., Ltd., was used as a high-speed stirrer. Stator, turbine, and vessel of the mixer were the same as those used in the previous experiment,<sup>3</sup> while gear for acceleration was exchanged by a belt.

### **Method of Stirring**

The solution, 200 ml, was divided into two parts of 10 ml and 190 ml, respectively, and the larger part was placed in a 300-ml vessel. The vessel was attached to the homomixer and placed in a water bath for cooling. The solution was then stirred at a speed of 30,000 rpm. Considerable heat was generated during stirring, and the temperature of the solution rose on account of the low efficiency of cooling. Considerable heat was also generated by the rotating parts of the mixer. For keeping the temperature of the solution within a certain range (20°C) and to conserve the mixer, 5-min stirring and 10–15-min pauses for cooling were alternated. After stirring for a given time, about 10 ml of the stirred solution was taken out and stirring was continued.

### **Polymer Separation**

In the case of poly(ethylene oxide) solution, the polymer was recovered by drying the removed solution by a hot-air drier until its weight became constant. In the case of poly(methyl methacrylate), stirred solution was poured into excess methanol and poly(methyl methacrylate) was precipitated. The precipitant was filtered off and dried with air. Percentage of recovered polymer was at least 98.7%, and poly(methyl methacrylate) was almost completely precipitated with methanol.

In the case of solution containing both poly(ethylene oxide) and poly(methyl methacrylate), a solution containing both of them at a weight ratio of 50:50 was prepared and the following method of separation was tested. The solution was poured into a large quantity of methanol to precipitate a polymer, which was filtered off and dried. One polymer was thus obtained. The filtrate was dried by a hot-air drier to constant weight to obtain another polymer. The weight ratio of the recovered polymers was 52:48. It was confirmed by IR spectra that the former was poly(methyl methacrylate) and that the latter was poly(ethylene oxide). It is considered that errors in intrinsic viscosities of polymers thus separated are not large. As a result, the polymers in the solution containing poly(ethylene oxide) and poly(methyl methacrylate) were separated by this method.

### Method of Measuring Viscosity

Intrinsic viscosities of polymers recovered in benzene were measured at 30°C with an Ubbelohde viscometer.

## RESULTS

### Stirring of Poly(ethylene Oxide) Solution

Benzene solutions containing 1–4% w/v of poly(ethylene oxide) were prepared (2–8 g polymer was dissolved in 200 ml benzene) and stirred at a speed of 30,000 rpm. Stirred solutions were dried with air to obtain the polymer. Viscosities were measured. Changes in intrinsic viscosity versus stirring time are shown in Figure 1. Rate of decrease in viscosity is large at first, then becomes small and seems to reach a constant value. When the figure is observed as a whole, a certain tendency with change in concentration cannot be found. This is in complete agreement with the results of our previous paper.<sup>3</sup> Loss of solvent due to the heat generation with high-speed stirring occurred and caused a change in concentration during stirring. Concentrations of solutions before stirring and 5, 20, 40, 60, and 90 min after stirring were, respectively, 1.21, 1.24, 1.32, 1.27, 1.33, and 1.39% w/w for 1% w/v solution (where 2 g polymer was dissolved in

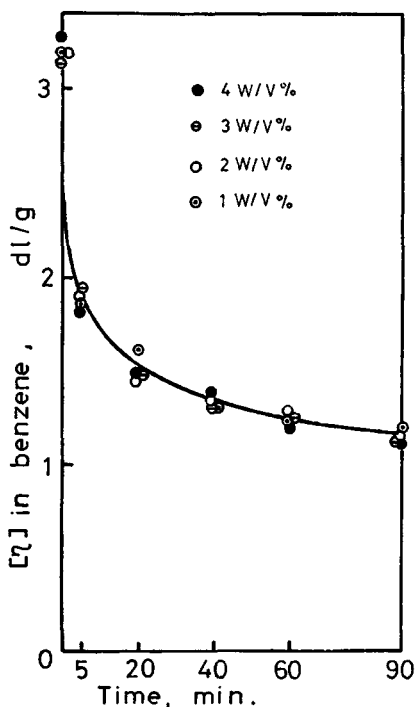


Fig. 1. Degradation of poly(ethylene oxide) (PEO) with high-speed stirring in PEO-benzene system (30,000 rpm, 20°C).

200 ml benzene); 2.34, 2.38, 2.42, 2.46, 2.52, and 2.65% w/w for 2% w/v solution (where 4 g polymer was dissolved in 200 ml benzene); 3.38, 3.44, 3.58, 3.74, 3.85, and 3.90% w/w for 3% w/v solution (where 6 g polymer was dissolved in 200 ml benzene); and 4.95, 4.87, 5.12, 5.41, 5.72, and 5.94% w/w for 4% w/v solution (where 8 g polymer was dissolved in 200 ml benzene). With increase in concentration, the change in concentration became larger. But the effect of the change in concentration during stirring on the rate of degradation is negligible because little difference in the rate of decrease in intrinsic viscosity appeared with change in concentration ranging 1–4% w/v as shown in Figure 1.

### Stirring of Poly(methyl Methacrylate)

Benzene solutions containing 1–4% w/v of poly(methyl methacrylate) were prepared (2–8 g polymer was dissolved in 200 ml benzene) and stirred at a speed of 30,000 rpm. Polymer solutions stirred for a given time were poured into a large amount of methanol. Polymers insoluble in warm methanol were separated, dried with air, and submitted to measurement of intrinsic viscosity. Changes in intrinsic viscosity versus stirring time are shown in Figure 2. Decrease in viscosity was large for 1% w/v solution, but a certain tendency with change in concentration cannot be found.

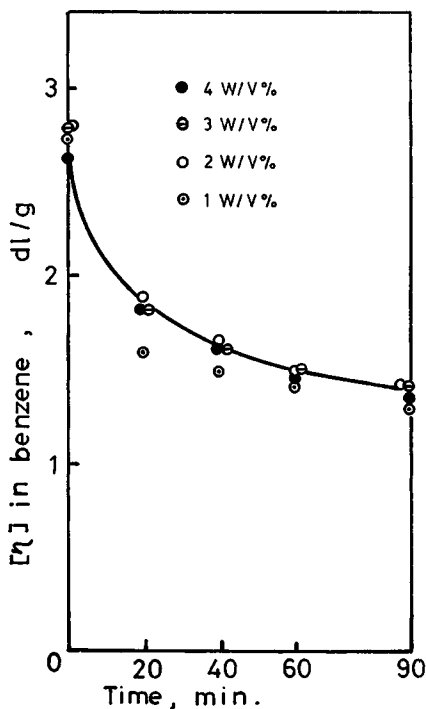


Fig. 2. Degradation of poly(methyl methacrylate) (PMMA) with high-speed stirring in PMMA-benzene system (30,000 rpm, 20°C).

The rate of degradation was not affected with change in concentration of solution. Concentrations of solutions before stirring and 20, 40, 60, and 90 min after stirring were, respectively, 1.10, 1.14, 1.17, 1.17, and 1.19% w/w for 1% w/v solution; 2.25, 2.25, 2.32, 2.36, and 2.34% w/w for 2% w/v solution; 3.28, 3.38, 3.55, 3.69, and 3.84% w/w for 3% w/v solution; and 4.15, 4.41, 4.71, 4.05, and 5.06% w/w for 4% w/v solution. The effect of the change in concentration during stirring is negligible, as shown in the previous section.

### Stirring of Solution Containing Both Poly(ethylene Oxide) and Poly(methyl Methacrylate)

Solutions containing 2 and 6 g, 4 and 4 g, or 6 and 2 g poly(ethylene oxide) and poly(methyl methacrylate), respectively, in 200 ml benzene were prepared (total concentrations of poly(ethylene oxide) and poly(methyl methacrylate) were made 4% w/v and ratio of the polymers was changed) and stirred at a speed of 30,000 rpm. Polymer solutions stirred for a given time were poured into a large amount of methanol. The polymer insoluble in warm methanol, poly(methyl methacrylate), was separated, dried with air, and submitted to measurement of intrinsic viscosity. Filtrates were dried with warm air to constant weights, to recover

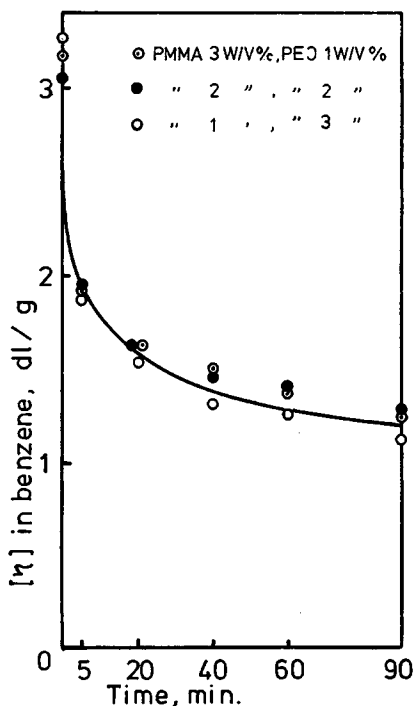


Fig. 3. Degradation of PEO with high-speed stirring in PEO-PMMA-benzene system (30,000 rpm, 20°C).

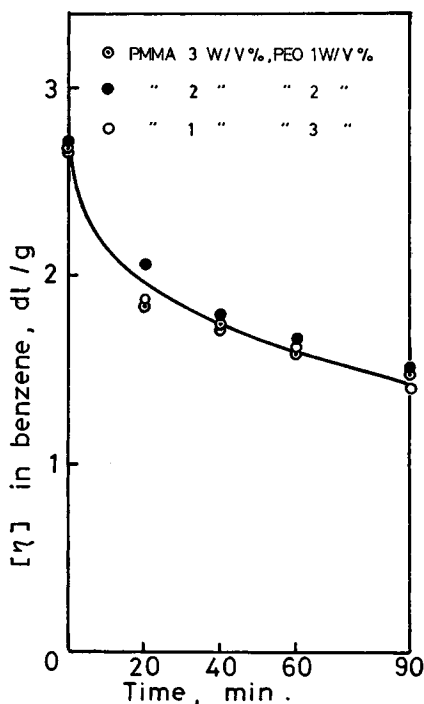


Fig. 4. Degradation of PMMA with high-speed stirring in PEO-PMMA-benzene system (30,000 rpm, 20°C).

another polymer, poly(ethylene oxide). It was also submitted to measurement of intrinsic viscosity. Changes in intrinsic viscosity of poly(ethylene oxide) versus stirring time are shown in Figure 3 and those of poly(methyl methacrylate), in Figure 4. Concentrations of solutions before stirring and 5, 20, 40, 60, and 90 min after stirring were, respectively, 4.36, 4.36, 4.68, 4.91, 5.21, and 5.34% w/w total for both polymers for the solution containing 3% w/v of poly(ethylene oxide) and 1% w/v of poly(methyl methacrylate); 4.60, 4.67, 4.98, 5.15, 5.35, and 5.55% w/w for the solution containing 2% w/v of each polymer; and 4.40, 4.54, 4.84, 5.21, 5.52, and 5.65% w/w for the solution containing 1% w/v and 3% w/v of both polymers, respectively. The effect of the change in concentration during stirring is negligible, as shown in a previous section. Respective intrinsic viscosities of poly(ethylene oxide) and poly(methyl methacrylate) were similarly decreased in spite of the change in ratio of poly(ethylene oxide) to poly(methyl methacrylate), and no dependency can be found.

## DISCUSSION

Benzene solutions containing different amounts of poly(ethylene oxide) were stirred at a high speed, and the intrinsic viscosities of the polymers recovered from the solutions were measured. The intrinsic viscosities were rapidly decreased at first and slowly decreased with stirring time.

The appearance of the decrease in viscosity was similar, regardless of change in solution concentrations within the range 1–4% w/v (Fig. 1). The same was found for poly(methyl methacrylate) (Fig. 2). Poly(ethylene oxide)–poly(methyl methacrylate)–benzene systems (no phase separation was found in the concentration range applied to the experiment) were stirred, and the appearance of decrease in intrinsic viscosity of recovered poly(ethylene oxide) was compared with that from poly(ethylene oxide)–benzene system. No clear difference was found regardless of difference in system (compare Fig. 1 with Fig. 3). The same was found for poly(methyl methacrylate) (compare Fig. 2 with Fig. 4). The results confirmed that polymer concentration did not affect the rate or the degree of decrease in intrinsic viscosity.

Polymer chains rupture to decrease intrinsic viscosity when polymer solution is stirred at high speed. Therefore decrease in intrinsic viscosity may be used as a parameter of the scission of polymer chains. The concentration of polymer solutions and polymer chains of different species which were mixed did not affect the rate or degree of decrease in intrinsic viscosity. Studies on the effect of polymer concentrations on the degradation by ultrasonic waves or high-speed stirring revealed the following. Schmidt and co-workers<sup>13</sup> carried out such experiments using solutions of polystyrene in toluene. They observed that the effect of ultrasonic waves diminished with increasing polymer concentrations and that degradation ceased altogether when the concentration became so high that the solution was of a gel-like consistency.

The rate of degradation of polystyrene by ultrasonic waves as a function of concentration of the polymer was investigated by Jellinek and co-workers<sup>14</sup>;  $\Delta P_w/P_n$  (where  $\Delta P_w$  is the decrease in weight-average chain length after 0.25 hr of exposure and  $P_n$  is the initial chain length) as a measure of the overall rate constant was plotted against the logarithm of the concentration. Excepting the case of low ultrasonic intensity, curves of  $\Delta P_w/P_n$  versus concentration were horizontally flat or slightly inclined.

According to the experiments of Grohn and co-workers<sup>10</sup> which were carried out on poly(methyl methacrylate) in chloroform, degradation by high-speed stirring was larger with decreasing concentration of the polymer. Similar results were obtained by Goto and co-workers<sup>16</sup> for the degradation of poly(vinyl acetate) in cyclohexane, the polymer concentration ranging 1.2–4% w/v.

It was a common result that the increase in concentration did not promote the degradation of polymer chains. The increase in concentration of polymers did not affect or decrease the rate and the extent of rupture of polymer chains.

From our experimental results and those of others it appears that adjacent polymer chains, except a rupturing polymer chain, do not affect polymer chain scission regardless of the polymer species. If an adjacent polymer chain had been associated with the rupture of a polymer chain, the effect of polymer concentration would have been positive because the



possibility of association between a polymer chain and an adjacent polymer chain is increased with increasing concentration.

Two theories can be considered for the mechanism of scission of polymer chains due to the effect of mechanical forces on polymer solution. One is the theory that interaction between polymer chain and solvent brings about scission, and the other is that interaction between polymer chains, such as entanglement and collision, causes the rupture. The results obtained in the experiment (1-4% w/v concentration range) seem to directly show that the latter mechanism is not predominant. If the latter mechanism were the case, the rate of scission would be increased with increasing concentration of total polymers. If interaction between polymer chains were necessary to the rupturing process, the concentration of polymers would affect scission exponentially. Therefore, the proportion of change in concentration applied, which was fourfold at its largest, is considered to have been not very large, but sufficient.

Arai and co-workers<sup>11</sup> suggested, from experimental results on polystyrene, that the scission of polymer chain in solution in the concentration range 1-2% w/w was not caused by entanglement but rather by force of friction on the chain. The authors' experimental results clearly show that the effect of interaction between polymers is insignificant.

Harrington<sup>16</sup> has concluded from the agreement of hydrodynamic theory with experimental data that limiting molecular degradation with high-speed stirring of special thin, highly sharpened blades occurred in the boundary layer region on the surface of blades; that intense velocity gradients existing in the boundary layer near the leading edge of the blades led to the development of tensile forces on the molecules which, operating through intramolecular displacements, provided a mechanical activation energy for chain scission; and that polymer chains breaking in a hydrodynamic shear field were completely extended along the streamlines of flow. It is hardly considered that there is an effect of interaction between a breaking polymer chain and another chain in such hydrodynamic shear field. Since the shape of the rotor of the homomixer is not the same as that of the blade of Harrington's mixer, the effect of turbulent flow or cavitation besides laminar flow might be considered in the experiment. The fact, which has now been made clear, that the interaction between polymer molecules is not predominant seems to show either that turbulent flow or cavitation does not play an important role or that, if cavitation plays a role, no force of collision of fluid due to cavity collapse (namely, no force of collision of polymer molecules) but velocity gradients formed in the fluid act as rupturing forces. In a field with velocity gradients, some segments of a polymer chain which is extended to some extent move at high speed, but other segments move at another speed, producing a tensile force on the polymer chain. Therefore, entanglements of polymer chains are not always needed for producing the necessary inertia. It is reasonable to consider that scission of polymer molecules by high-speed stirring in 1-5% solutions is not caused by intermolecular interactions, such as

collision of molecules, but by intramolecular interaction, such as intramolecular displacement, due to velocity gradients during the degradation.

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