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Mechanochemical block copolymerization of poly(vinyl chloride) with methyl methacrylate by ultrasonic irradiation

Hideki Fujiwara and Kunio Goto

Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology,
16-1, Omiya 5-chome, Asahi-ku, Osaka, 535 Japan

SUMMARY

Mechanical degradation and mechanochemical block copolymerization in systems of poly(vinyl chloride)-methyl methacrylate-solvents have been studied by ultrasonic irradiation at 60 ℃. The effect of the concentrations of poly(vinyl chloride) on mechanical degradation was investigated. In addition, the effects of poly(vinyl chloride) and methyl methacrylate concentrations on mechanochemical block copolymerization were investigated. The rate equation for mechanochemical block copolymerization has been deduced, and the experimental results were in fairly good agreement with the equation. The changes in the composition of the block copolymer and homopolymers in the reaction products were followed by turbidimetric titration.

INTRODUCTION

Many studies of mechanical degradation of polymer chains in solution by ultrasonic irradiation have been reported (1-10).

On the other hand, the polymeric free radicals produced by the degradation of chains should be able to initiate vinyl copolymerizations. However, mechanochemical block copolymerization by ultrasonic irradiation has not been fully studied.

In earlier papers, the study was made of mechanochemical block copolymerizations of polystyrene-methyl methacrylate (11), polybutadiene-styrene (12), poly(vinyl chloride)-styrene (13), and poly(vinyl alcohol)-methyl methacrylate (14) by ultrasonic irradiation.

The present paper is concerned with mechanical degradation and mechanochemical block copolymerization in systems of poly(vinyl chloride)-methyl methacrylate-solvents effected by ultrasonic irradiation. In particular, we report on the kinetics of the block copolymerization and the composition of the block copolymer and homopolymers in the reaction products.

EXPERIMENTAL

Materials

Poly(vinyl chloride) PVC (2B-719, Teijin Co. Ltd.) was purified by extraction with hot pure methanol for 80 hr. The number-average degree of polymerization was 1,530.

The methyl methacrylate monomer MMA was washed successively with sodium bisulfite solution, sodium hydroxide solution, and sodium chloride solution. After drying over anhydrous sodium sulfate, the monomer was filtered and purified by distillation under reduced pressure in a stream of nitrogen.

Purified tetrahydrofuran THF and cyclohexanone CHAO were used as polymerization solvents.

Purified methanol was used as the precipitating agent.

Apparatus and Procedures

An ultrasonic generator (Model USV-150V, Cho-Onpa Kogyo Co. Ltd.) equipped with an electrostrictive barium titanate vibrator of diameter 6.0 cm and thickness 1.2 cm was used. The output of the vibrator had an intensity of 7.4 watts/cm^2 at a constant frequency of 200 kHz.

In the procedure for mechanical degradation, PVC was dissolved in THF containing *p*-benzoquinone inhibitor at 40 ℃, and then MMA was added slowly to the solution with stirring at -10 ℃. Ten mililiters of the solution were poured into a 25 ml special glass reaction vessel, which was then degassed and sealed under one atmospheric pressure of dry nitrogen. Ultrasonic irradiation of the polymer solution was carried out for 10, 20, 30, 40, 50, and 70 min at 60 ℃. The distance between the surface of the vibrator and the center of the bottom of the sealed reaction vessel was 9.2 mm. After reaction, the solution was poured into a large amount of methanol containing *p*-benzoquinone. The precipitated polymer was filtered, washed, and dried in vacuo at 45 ℃, and then the weight of the polymer was measured. The number-average degree of polymerization at various stages of mechanical degradation was determined by osmometry.

Mechanochemical block copolymerization of PVC-MMA-solvents systems was carried out by the irradiation in the absence of *p*-benzoquinone. The conversion was calculated from the weight of the polymer produced by the copolymerization. The composition of the copolymer and homopolymers in the reaction products was determined by turbidimetry.

Measurement of Osmotic Pressures

The osmotic pressures of the polymers were measured in THF with an electronic membrane osmometer (K. G. Dr.-Ing. Herbert Knauer GmbH) at 30 ℃.

Determination of Turbidities

The solution turbidities of the samples were determined with a turbidimetric titrator (Model NT-3, Kotaki Works Co. Ltd.) at 30 ℃. The solvent and precipitating agent were THF and distilled water, respectively. The polymer concentration was 0.10 g/l.

RESULTS AND DISCUSSION

Mechanical Degradation and Mechanochemical Block Copolymerization

Mechanical degradation curve, number-average degree of polymerization $\bar{P}_n$ of PVC versus irradiation time, obtained by ultrasonic irradiation is shown in Figure 1. The values of

$\bar{P}_n$ decrease with irradiation time, and the curve represents fitting by the rate equation for mechanical degradation was derived previously (15, 16).

$$\frac{1}{P_t - P_\infty} = k_s t + \frac{1}{P_0 - P_\infty} \quad (1)$$

where P_0, P_t, and P_∞ are, respectively, the degree of polymerization of the polymer at time $t = 0$, at any time t, and at the final stage of the degradation process; k_s is a rate constant.

The theoretical curve is in agreement with the experimental values. In addition, the rate of decrease in $\bar{P}_n$ of the degraded polymer is not dependent on PVC concentration within the 0.120 to 0.200 mol/l range. However, the number of chain scissions N should be greater at the higher concentration.

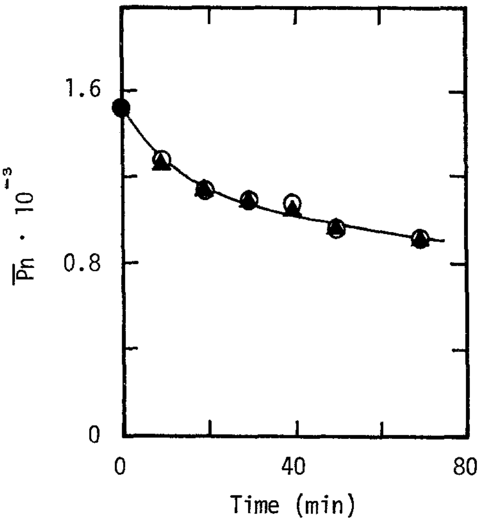
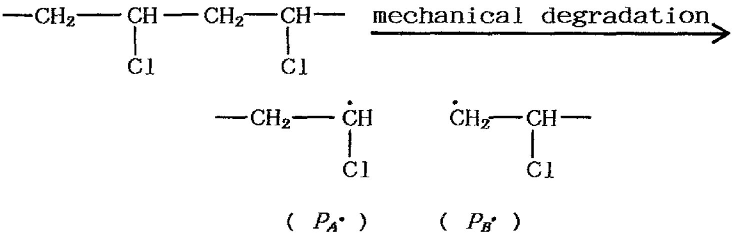


Figure 1. Mechanical degradation of PVC by ultrasonic irradiation: points determined by experiment, a curve calculated from eq. (1). [PVC]: (○),0.200 mol/l; (▲),0.120 mol/l. [MMA]: 2.67 mol/l. [THF]: 7.93 mol/l. [CHAO]: 0 mol/l. [p-Benzoquinone]: 0.242 mol/l.

Two radicals of PVC resulted from ultrasonic degradation as follows:



$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \xrightarrow{\text{mechanical degradation}} \underset{(P_A\cdot)}{-CH_2-\underset{Cl}{\dot{C}H}} \qquad \underset{(P_B\cdot)}{\dot{C}H_2-\underset{Cl}{CH}-}$$

Mechanochemical copolymerization of MMA is initiated by these polymeric radicals. However, this copolymerization was found to be completely inhibited in the presence of p-benzoquinone.

The effects of PVC and MMA concentrations on mechanochemical block copolymerization are shown in Figures 2 and 3. The rates of copolymerization clearly increase with increasing PVC and MMA concentrations. When the solution, in the absence of PVC, was subjected to ultrasonic irradiation, the polymerization of MMA did not occur.

Since the active two types of PVC are responsible for the initiation of copolymerization, the rate of mechanochemical block copolymerization in systems of PVC-MMA-solvents is derived from the following sequence of elementary reactions:

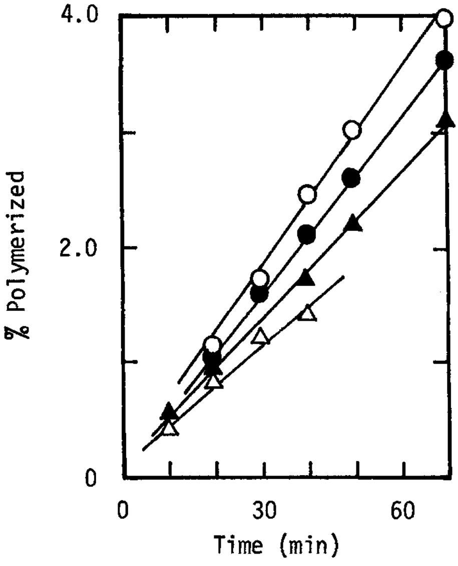


Figure 2. Effect of PVC concentrations on mechanochemical copolymerization. [PVC]: (○),0.205 mol/l; (●),0.172 mol/l; (▲),0.153 mol/l; (△),0.121 mol/l. [MMA]: 2.73 mol/l. [THF]: 8.08 mol/l. [CHAO]: 0 mol/l.

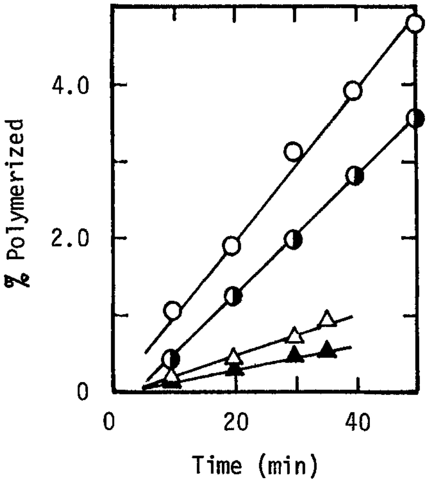


Figure 3. Effect of MMA concentrations on mechanochemical copolymerization. [MMA]: (○),1.38 mol/l; (◑),0.931 mol/l; (△),0.434 mol/l; (▲),0.229 mol/l. [PVC]: 0.190 mol/l. [CHAO]/[THF]= 0.735.

$$PVC \xrightarrow{k_d} P_A \cdot + P_B \cdot$$ mechanical degradation

$$\left.\begin{array}{l} P_A \cdot + M \xrightarrow{k_{i,A}} P_A\text{—}M \cdot \\ P_B \cdot + M \xrightarrow{k_{i,B}} P_B\text{—}M \cdot \end{array}\right\}$$ initiation

$$\left.\begin{array}{l} P_A\text{—}M \cdot + M \xrightarrow{k_p} P \cdot \\ P_B\text{—}M \cdot + M \xrightarrow{k_p} P \cdot \end{array}\right\}$$ propagation

$$P \cdot + M \xrightarrow{k_{tr,M}} P + M \cdot$$ chain transfer to MMA

$$P \cdot + P_i \xrightarrow{k_{tr,P}} P + P_i \cdot$$ chain transfer to polymer

$$P \cdot + THF \xrightarrow{k_{tr,T}} P + THF \cdot$$ chain transfer to THF

$$P\cdot \; + \; CHAO \xrightarrow{k_{tr,C}} P \; + \; CHAO\cdot$$ chain transfer to CHAO

$$P_x\cdot \; + \; P_y\cdot \xrightarrow{k_t} P_{x+y}\;,\; P_x + P_y$$ termination

where k_d, $k_{i,A}$, $k_{i,B}$, k_p, $k_{tr,M}$, $k_{tr,P}$, $k_{tr,T}$, $k_{tr,C}$, and k_t are rate constants for the respective reactions. When chain transfer reactions to THF and / or CHAO are much faster than the termination reaction, the initial rate of mechanochemical block copolymerization R_p is given by:

$$\frac{1}{R_p\,[\mathrm{THF}]} = \frac{1}{k_d f\,[\mathrm{PVC}][\mathrm{MMA}]}\left\{\frac{k_{tr,T}}{k_p} + \frac{k_{tr,C}\,[\mathrm{CHAO}]}{k_p\,[\mathrm{THF}]}\right\} \qquad (2)$$

where [PVC] and [MMA] are the initial concentrations of PVC and MMA. [THF], [CHAO], and f are the concentrations of THF and CHAO and the initiation efficiency of the active end radicals of PVC. The results from equation (2) are shown in Figures 4 and 5, where the relationships between −{ln R_p + ln [THF]} and −ln [PVC] in Figure 4 and between −{ln R_p + ln [THF]} and −ln [MMA] in Figure 5 are respectively illustrated. As is obvious from these figures, the linear functions are found in conformity with mechanochemical block copolymerization. In addition, each value of the slopes of the straight line in Figures 4 and 5 was 1.0. Accordingly, the

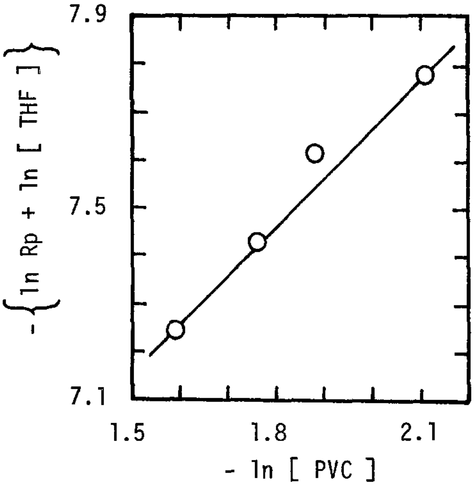


Figure 4. Relationship between −(ln R_p + ln [THF]) and −ln [PVC] for mechanochemical block copolymerization of MMA with PVC. [MMA]: 2.73 mol/l. [THF]: 8.08 mol/l. [CHAO]: 0 mol/l. (R_p : mol/l s).

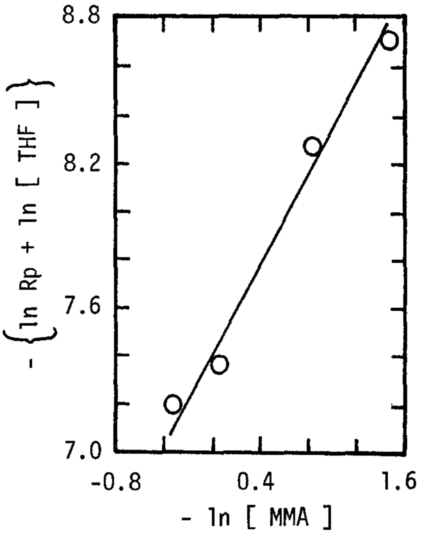


Figure 5. Relationship between −(ln R_p + ln [THF]) and −ln [MMA] for mechanochemical block copolymerization of MMA with PVC. [PVC]: 0.190 mol/l. [CHAO]/[THF]= 0.735. (R_p : mol/l s).

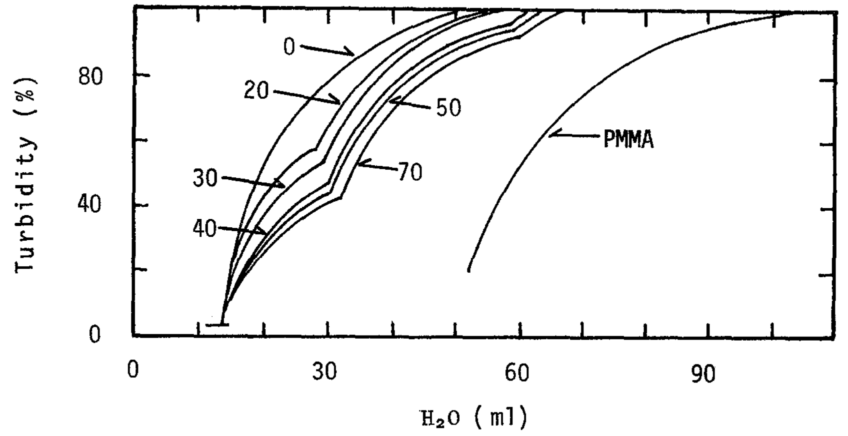


Figure 6. Turbidimetric titration curves at various stages during mechanochemical block copolymerization. Samples ([PVC]: 0.172 mol/l. [MMA]: 2.73 mol/l. [THF]: 8.08 mol/l. [CHAO]: 0 mol/l): (0), PVC sample; (20), 20 min treatment; (30), 30 min treatment; (40), 40 min treatment; (50), 50 min treatment; (70), 70 min treatment. (PMMA), PMMA produced by emulsion polymerization at 60 ℃.

initial rate of mechanochemical block copolymerization R_p is given by $1 / R_p\,[\mathrm{THF}] \propto 1 / [\mathrm{PVC}][\mathrm{MMA}]$.

Changes in the Composition of the Block Copolymer and Homopolymers in the Reaction Products

The turbidimetric titration curves at various stages of the block copolymerization are shown in Figure 6. The curve of the original PVC has a smooth *S* shape, but those of the samples after the block copolymerization are inflected. In particular, the curves of the samples after 40 min or above have two inflection points. This suggests that the samples consist of ternary systems of PVC, the block copolymer of MMA with PVC, and poly(methyl methacrylate) PMMA.

The changes in the composition of the block copolymer and homopolymers in the

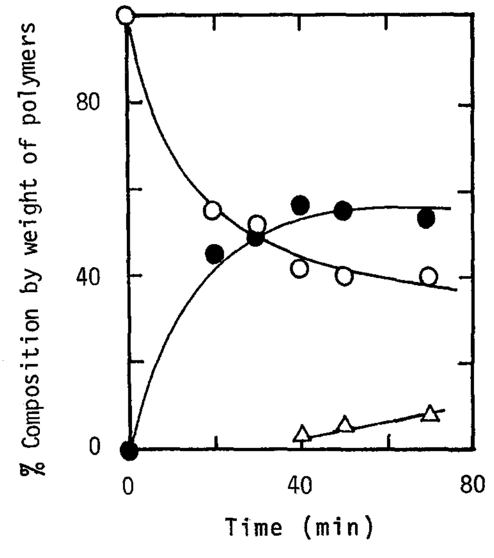


Figure 7. Changes in the composition of the block copolymer and homopolymers in the reaction products. Samples ([PVC]: 0.172 mol/l. [MMA]: 2.73 mol/l. [THF]: 8.08 mol/l. [CHAO]: 0 mol/l): (○), PVC; (●), block copolymer; (△), PMMA.

reaction products with respect to the irradiation time are shown in Figure 7. The compositions of the polymers were calculated respectively from differential titration curves derived from Figure 6. The weight proportion of PVC decreases with the progress of the block copolymerization, but that of the block copolymer increases. In addition, the formation of PMMA after 40 min or above is thought to occur since the MMA segment in the block copolymer undergoes mechanical degradation during the irradiation and the chain transfer reaction to MMA occurs.

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