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Mechanochemical synthesis and characterization of poly(vinyl chloride)-*block*-poly(ethylene-*co*-propylene) copolymers by ultrasonic irradiation

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Summary

Mechanical degradation and mechanochemical reaction in heterogeneous and homogeneous systems of poly(vinyl chloride) and poly(ethylene-*co*-propylene) polymer have been studied by ultrasonic irradiation at 30 °C. The rates of decrease in the number-average molecular weights of the degraded poly(vinyl chloride) and poly(ethylene-*co*-propylene) polymer were much faster in order of the solid poly(vinyl chloride)–poly(ethylene-*co*-propylene) polymer solution, the swelled poly(vinyl chloride)–poly(ethylene-*co*-propylene) polymer solution, and the homogeneous solution systems. On the other hand, mechanochemical reaction occurred by free radicals produced from the chain scissions of both polymers by ultrasonic waves. The changes in the composition of the total block copolymer, the unreacted poly(vinyl chloride), and the unreacted poly(ethylene-*co*-propylene) polymer in individual reaction systems were obtained. In addition, the microscopic observation of the surfaces of the polymers on before and after mechanochemical reaction is carried out.

Introduction

Poly(vinyl chloride) has various characteristics, but the impact resistance is generally poor. Therefore, the reforming of that impact characteristic was studied by the use of polymer blend technique (1–4). For example, the blending systems of poly(vinyl chloride) and the elastomer of poly(acrylic acid ester) (1) or the chlorinated acrylonitrile–butadiene rubber (2) have been carried out. As noted above, a marked development of the thermoplastic elastomers of poly(vinyl chloride) is performed through the polymer blend technique. However, mechanochemical synthesis of the thermoplastic elastomers of poly(vinyl chloride) by ultrasonic irradiation has not been entirely studied. Therefore, the author has used an ultrasonic waves for the synthesis of mechanochemical block copolymer as one of such elastomers and attended to poly(ethylene-*co*-propylene) polymer that is excellent in chemical resistance and aging resistance. In earlier paper, the study of mechanochemical synthesis of poly(vinyl chloride)−*block*−poly(vinyl alcohol) copolymers in heterogeneous systems by ultrasonic irradiation was shown (5).

The present paper is concerned with mechanochemical reactions in heterogeneous and homogeneous systems of poly(vinyl chloride) and poly(ethylene-*co*-propylene) polymer affected by ultrasonic irradiation.

Experimental

Materials

Suspension polymerized poly(vinyl chloride) sample PVC (Kane Vinyl XS-4000, Kanegafuchi Chemical Industry Co., Ltd.) was purified by extraction with hot pure benzene and methyl alcohol for 80 hr. The average particle diameter D of PVC and the porosity P in the PVC-grain particle were 150 μm and 0.640 ml Hg/g PVC. The number-average molecular weight $\bar{M}_n$ of PVC determined by gel permeation chromatography was 1.72×10^5. Poly(ethylene-*co*-propylene) polymer EPM (EP961 SP, JSR Co., Ltd.) was purified by the use of *o*-xylene−methyl alcohol system. The ethylene and propylene contents bonded in EPM were 77.0 wt% and 23.0 wt% (0.833 mol vs. 0.167 mol) and the number-average molecular weight $\bar{M}_n$ was 1.50×10^5. Purified *o*-xylene was used as the reaction solvent by considering the specific acoustic impedance for the solid PVC and the solubility of EPM. Purified tetrahydrofuran THF was used as the reaction solvent and the solvents for the determinations of the solution turbidity and the $\bar{M}_n$ of polymers. Purified methyl alcohol was used as a precipitating agent.

Apparatus and Procedures

Two types ultrasonic generator (Model USV-150V and UE-200Z 26S-1A, Cho-Onpa Kogyo Co.,Ltd.) have been used for mechanical degradations and mechanochemical reaction of both polymers. The USV-150V generator was equipped with a stepped horn of stainless steel on a magnetostrictive nickel vibrator of 25 kHz and the UE-200Z26S-1A generator was equipped with an electrostrictive PZT vibrator of 26 kHz. The output powers of these generators had respectively the intensities of 150 watts and 200 watts. When an ultrasonic waves from the upper part of the reaction system was irradiated, the USV-150V generator has been used and the stepped horn of stainless steel on the vibrator was contacted on the surface of the solution. On the other hand, the PZT vibrator of the UE-200Z26S-1A generator has been used for the irradiation from the lower part of the reaction system and the center of the bottom of the reaction vessel was contacted on the surface of the vibrator.

The experiments of three kinds for mechanical degradations and mechanochemical reaction of both PVC and EPM were carried out in the following manner.

Experiment No. I: Solid PVC−EPM solution system

In a typical run for mechanical degradation, 2.00 g of the solid PVC, 80.0 ml of EPM−*o*-xylene solution (EPM: 0.800 g), and 1.60 g of *p*-benzoquinone inhibitor were poured into a

300 ml special glass reaction vessel. Ultrasonic irradiation was carried out for 60, 120, 180, 240, 300, and 360 min at the same time from the upper and the lower parts of the reaction system under one atmospheric pressure of dry nitrogen at 30 ± 0.1 °C. After the reaction, the solution was poured into a large amount of methyl alcohol containing *p*-benzoquinone inhibitor. The precipitated polymer was filtered, washed, and dried in vacuo at 40 °C. The degraded PVC and EPM were fractionated by the use of *o*-xylene at 80 °C. The number-average molecular weights $\bar{M}_n$ of PVC and EPM at various stages of the degradation were determined by gel permeation chromatography.

On the other hand, mechanochemical reaction of both PVC and EPM was carried out by the irradiation of the solid PVC–EPM solution in the absence of *p*-benzoquinone. The reaction products were fractionated by the use of *o*-xylene at 80 °C. Infrared spectra of the *o*-xylene–insoluble and the *o*-xylene–soluble polymers were determined by the cast film technique from THF solution with a Shimadzu FTIR-8600PC spectrophotometer. The compositions of the block copolymer, unreacted PVC, and unreacted EPM in the fractionated polymers were determined by turbidimetry (5, 6).

Experiment No. II: Swelled PVC–EPM solution system

In this reaction system, the mixture solvent of *o*-xylene/THF (1.0 vol. vs. 1.0 vol.) has been used for the purpose of swelling of the PVC particle. The original PVC particle has consequently been expanded by a factor of 2.4.

Further, mechanical degradations, mechanochemical reaction of both PVC and EPM, and the extraction separations of the polymers were carried out in a similar manner as above procedures.

Experiment No. III: Homogeneous solution system

In this reaction system, THF has been used as a common solvent of both PVC and EPM. Further, mechanical degradations, mechanochemical reaction, and the extraction separations of the polymers were carried out in a similar manner as above Experiment No. I.

Determination of the Number-Average Molecular Weights

The number-average molecular weights $\bar{M}_n$ of PVC and EPM at various stages of mechanical degradation were determined by gel permeation chromatography (Model HLC-8020, Tosoh Co., Ltd.) at 40 °C. Two G2000HXL TSK gel-columns and one each of G3000HXL and G4000HXL were connected to series in this order. THF was used as a solvent and a flow rate was 1.0 ml/min. Molecular weights of polymers were calibrated with polystyrene standards.

Determination of Turbidities

The solution turbidities of the fractionated polymers were determined with a turbidimetric titrator (Model NT-301H, Kotaki Works Co., Ltd.) at 30 °C. In the case of the *o*-xylene–insoluble polymer, the solvent and the precipitating agent were THF and distilled water. The polymer concentration was 0.050 g/L.

On the other hand, the solvent and the precipitating agent for the *o*-xylene–soluble polymer were THF and methyl alcohol. The polymer concentration was 0.030 g/L.

In preference to the above determinations, the turbidities of various kinds of the dilute solutions of PVC and EPM were determined and the calibration curves to the individual polymers were made up from the polymer concentration and the area under the peak of the turbidimetric titration curve (5, 6). The proportions of the unreacted PVC, unreacted EPM, and the block copolymer were calculated by the use of these calibration curves.

Results and Discussion

Mechanical Degradation

The changes in the number-average molecular weights $\bar{M}_n$ of PVC and EPM with respect to the irradiation times on mechanical degradation are shown in Figure 1 and 2. The values of $\bar{M}_n$ of PVC and EPM decreased with irradiation times and these results show that the chain scissions of both polymers occurred at each reaction system. The rates of decrease in $\bar{M}_n$ of the degraded polymers were much faster in order of the solid PVC–EPM solution, the swelled PVC–EPM solution, and the homogeneous solution systems. In the case of the degradation of PVC, this result shows that the scission of PVC occurs vigorously with increasing the flexibility of PVC chain. Further, it is thought that the degradation of EPM is based on a difference in the extent of the broadening of EPM chain in solution, namely the difference in the flexibility of EPM chain. In general, mechanical degradation of polymers in solution by ultrasonic irradiation is known that polymer chain in good sol-

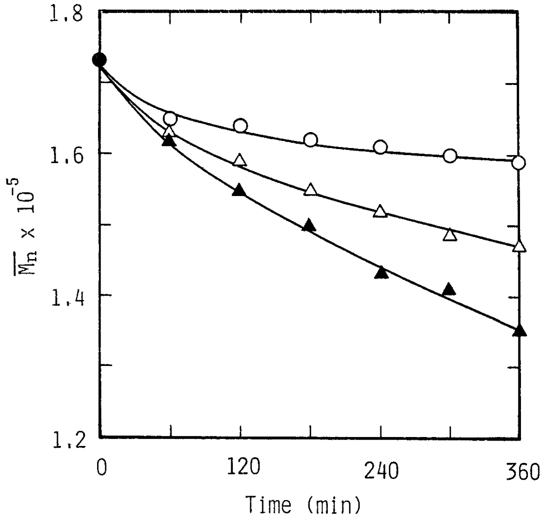


Figure 1. Mechanical degradation of PVC by ultrasonic irradiation. Reaction system: (○), Solid PVC—EPM solution; (△), Swelled PVC—EPM solution; (▲), Homogeneous solution.

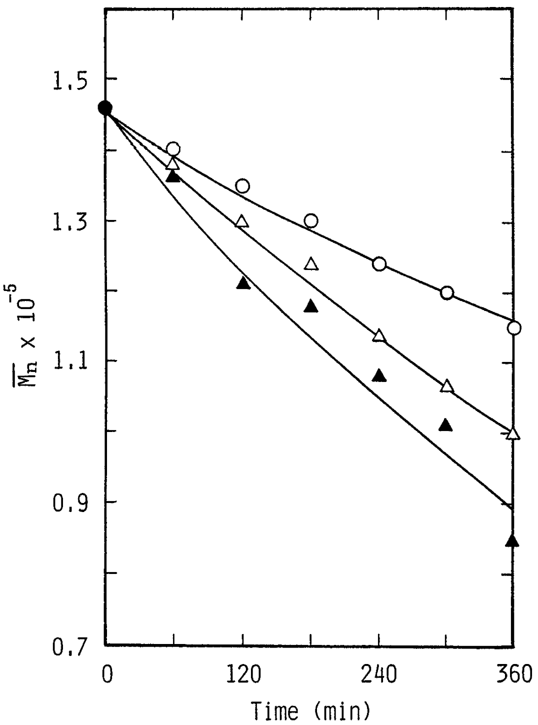
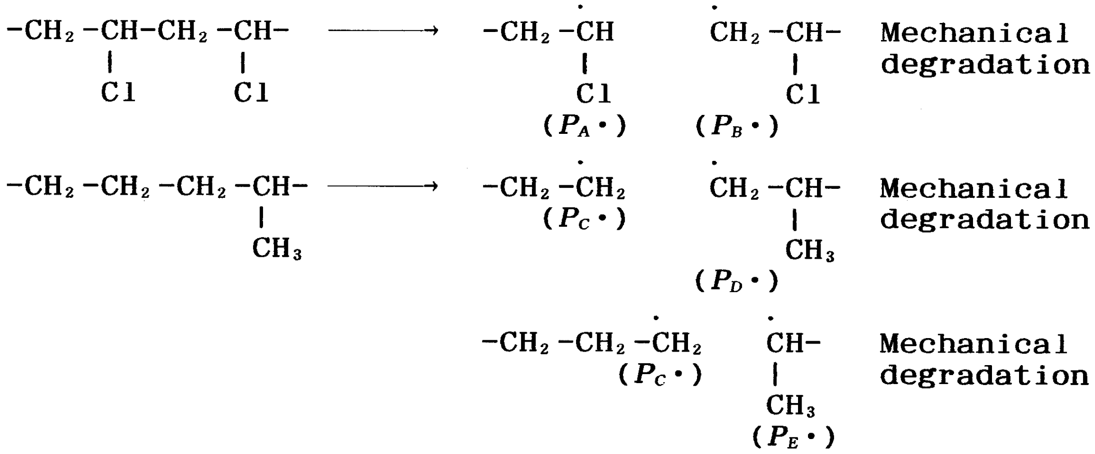


Figure 2. Mechanical degradation of EPM by ultrasonic irradiation. Reaction system: (○), Solid PVC—EPM solution; (△), Swelled PVC—EPM solution; (▲), Homogeneous solution.

vent is much more subject to scission than that in poor solvent (7). Accordingly, it is suggested that the broadening of EPM chain in THF is greater than in the case of *o*-xylene.

Mechanochemical Reaction

The end radicals of PVC and EPM resulted from mechanical degradation are expressed in the following manner and these active ends are responsible for the formation of mechanochemical PVC–block–EPM copolymer.



$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \longrightarrow \underset{(P_A\cdot)}{-CH_2-\underset{Cl}{\dot{C}H}} \quad \underset{(P_B\cdot)}{\dot{C}H_2-\underset{Cl}{CH}-} \quad \text{Mechanical degradation}$$

$$-CH_2-CH_2-CH_2-\underset{CH_3}{CH}- \longrightarrow \underset{(P_C\cdot)}{-CH_2-\dot{C}H_2} \quad \underset{(P_D\cdot)}{\dot{C}H_2-\underset{CH_3}{CH}-} \quad \text{Mechanical degradation}$$

$$\underset{(P_C\cdot)}{-CH_2-CH_2-\dot{C}H_2} \quad \underset{(P_E\cdot)}{\underset{CH_3}{\dot{C}H}-} \quad \text{Mechanical degradation}$$

Formation of PVC–*block*–EPM copolymers

$$P_A\cdot + P_C\cdot \longrightarrow P_A-P_C \qquad P_B\cdot + P_C\cdot \longrightarrow P_B-P_C$$

$$P_A\cdot + P_D\cdot \longrightarrow P_A-P_D \qquad P_B\cdot + P_D\cdot \longrightarrow P_B-P_D$$

$$P_A\cdot + P_E\cdot \longrightarrow P_A-P_E \qquad P_B\cdot + P_E\cdot \longrightarrow P_B-P_E$$

Infrared spectra of the *o*-xylene–insoluble and soluble polymers in the reaction product on the swelled PVC–EPM solution system are shown as examples in Figure 3 and 4.

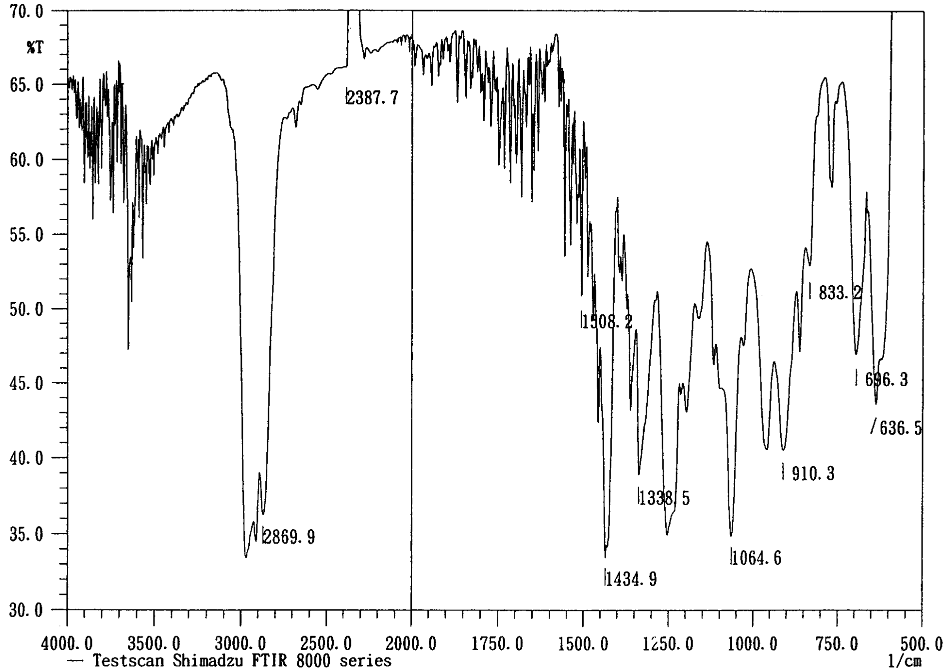


Figure 3. Infrared spectrum of the *o*–xylene—insoluble polymer in the reaction product on the swelled PVC—EPM solution system. Sample: 300 min treatment.

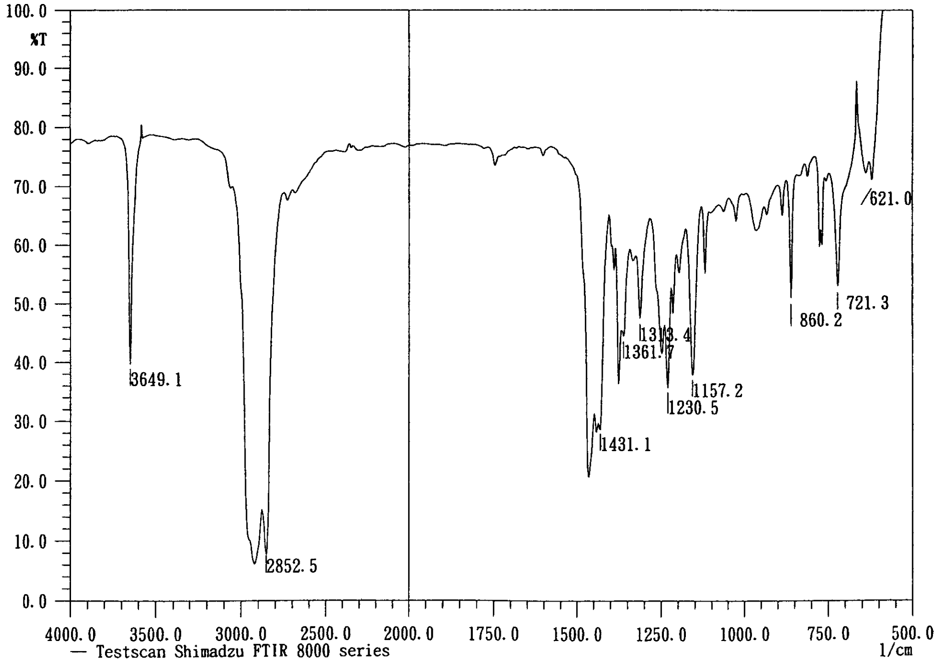


Figure 4. Infrared spectrum of *o*–xylene—soluble polymer in the reaction product on the swelled PVC—EPM solution system. Sample: 300 min treatment.

The absorption spectra due to the -CH_3 groups at 1377.1, 1467.7, and 2869.9 cm^{-1} with respect to the *o*-xylene–insoluble polymer in Figure 3 and the C-Cl bond at 621.0 cm^{-1} with respect to the *o*-xylene–soluble polymer in Figure 4 are respectively recognized. A similar result was observed for the absorption spectra of the *o*-xylene–insoluble and the *o*-xylene–soluble polymers in other reaction systems. These results indicate that the PVC–*block*–EPM copolymers are present as the mixtures together with an unreacted PVC in the *o*-xylene–insoluble polymer and an unreacted EPM in the *o*-xylene–soluble polymer.

The compositions of the total block copolymer, the unreacted PVC, and the unreacted EPM in the reaction products with respect to the irradiation time in various kinds of the reaction systems were obtained from the turbidimetric titration curves. Those results are shown in Figure 5. In the solid PVC–EPM solution system, the weight proportion of the total block copolymer increased up to 300 min, but that thereafter decreased. Within 300 min the proportion of the block copolymer is at the top of the reaction systems of three kinds of PVC and EPM. On the other hand, the proportions of the unreacted PVC and EPM decreased with increasing the time, but those values after 360 min increased. In particular, the significant increase in PVC was recognized. These results suggest that the vinyl chloride (VC) and the ethylene-propylene (EP) chains of the block copolymer underwent the scissions at the prolonged irradiation and the unreacted PVC and EPM are formed consequently. In this instance it may be said that a long VC chain of the block copolymer was much more subject to the vigorous scission than the EP chain of its copolymer. This is because mechanical degradation of PVC in the solid PVC–EPM solution system would not be so much caused (by reference to Figure 1) and the long VC chain was concerned with the formation of the block copolymer in the next mechanochemical reaction. In the swelled PVC–EPM solution system, the weight proportion of the total block copolymer increased with irradiation time and its value after 360 min did not decrease. On the other hand, the proportions of the unreacted PVC and EPM decreased with increasing the time, but the value of the unreacted EPM after 360 min increased slightly. In addition, the proportion of the unreacted EPM was slightly high than the case of the solid PVC–EPM solution system. These results suggest that the EP chain of the block copolymer underwent slightly the scission at the prolonged irradiation, but the scission of the VC chain of its copolymer did not occur. This is because the VC chain of the copolymer was shorter than the case of the solid PVC–EPM solution system. In the homogeneous solution system, the weight proportion of the total block copolymer was undoubtedly lower than the other reaction systems, its value decreased from 240 min, and the unreacted PVC and EPM, on the contrary, increased. Furthermore, the proportion of the unreacted PVC was relatively high and that of the unreacted EPM was relatively low than the other reaction systems. These results suggest that the scission of the VC chain of the block copolymer occurred vigorously from the initial step of the reaction, the unreacted PVC increased consequently, and the EP chain of the block copolymer was appreciably shorter than the other reaction systems. It is thought that the flexibilities of the polymer chains in the homogeneous solution system increase and

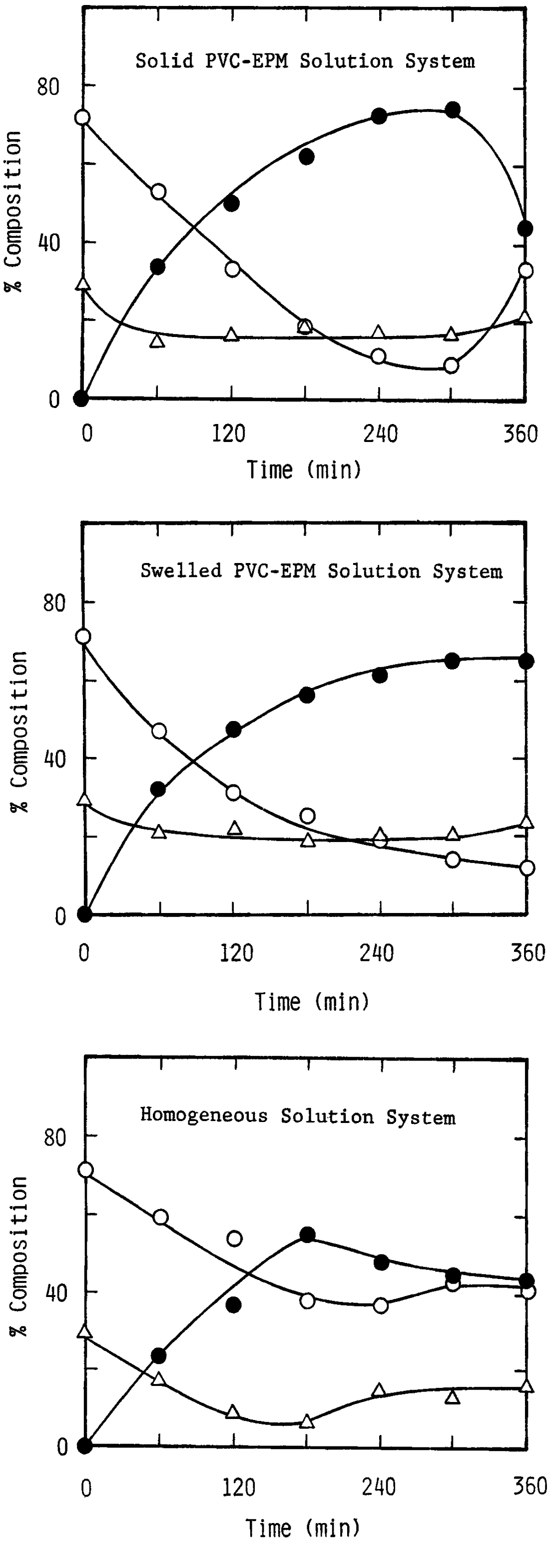
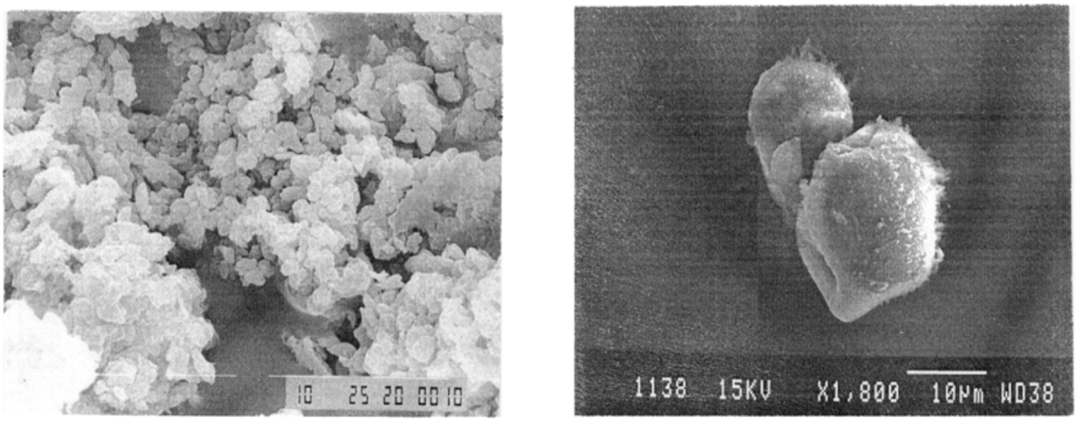


Figure 5. Changes in the composition of the total block copolymer and homopolymers in the reaction products in various kinds of the reaction systems. (●), Block copolymer; (○), PVC; (△), EPM.



(A) Primary particles in the grain of the original PVC
(B) *O*-xylene—insoluble polymer in the reaction product

Figure 6. Microscopic observations of the primary particles in the grain of the original PVC and the *o*-xylene—insoluble polymer after 300 min at the solid PVC—EPM solution system. Block copolymer content in the *o*-xylene—insoluble polymer: 86.9 wt%.

those chains are much more subject to mechanical degradation.

These results suggest that the synthesis of the block copolymers is no necessity for prolonged irradiation, the solid and the swelled PVC–EPM solution systems are preferred over the homogeneous solution system, and the VC and the EP segments in the block copolymer can be made to vary by changes in the experimental conditions.

The surfaces of the primary particles in the grain of the original PVC and the reaction product observed by a scanning electron microscope (Model JSM-840, Japan Electronics Co., Ltd.) are shown as example in Figure 6. The grain of the original PVC is formed as the aggregate of the primary particles and a small opening among the primary particles is present. On the other hand, the *o*-xylene–insoluble polymer had very different form in comparison with the primary particles of the original PVC. In particular, a downy polymer on that surface is recognized clearly.

Acknowledgments

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