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Mechanochemical block copolymerization in heterogeneous systems of the solid poly(vinyl chloride) with styrene by ultrasonic irradiation

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SUMMARY

Mechanochemical block copolymerization in heterogeneous systems of the solid poly(vinyl chloride)-styrene-sodium dodecyl sulfate aqueous solutions has been studied by ultrasonic irradiation at 65 °C. The block copolymerization of styrene was initiated by free radicals produced from the poly(vinyl chloride) particles by ultrasonic waves. The initial rate of the block copolymerization Rp was given by $Rp \propto [\text{Styrene}]\,[\text{Sodium dodecyl sulfate}]^{\frac{1}{2}}$. Both copolymer and homopolymer were obtained. For example, when 2.506 g of the poly(vinyl chloride) particles, 24.23 g of styrene, and 54.00 g of sodium dodecyl sulfate aqueous solution (0.500 wt%) were added in the reaction system, the weight proportions of the block copolymer and polystyrene after 60 min were approximately 50 and 20 %.

INTRODUCTION

Poly(vinyl chloride) and polystyrene are widely used in all the world. Poly(vinyl chloride) is not excellent in moldability, but polystyrene is excellent in it. When poly(vinyl chloride) has the better side of the moldability of polystyrene, the decrease in the costs of its molding and fabricating has become feasible. The improvement in this defect of poly(vinyl chloride) appears to be a possibility with the aid of mechanical blending of poly(vinyl chloride) and polystyrene by open two rolls or solution blending. However, the compatibility of both polymers was very poor in these blending systems (1, 2).

In earlier paper, the study of the coordinating function of vinyl chloride-*b*-styrene copolymers in mechanical blending of poly(vinyl chloride) and polystyrene by open two rolls was shown (1). Vinyl chloride-*b*-styrene copolymers were shown to be effective in coordinating these homopolymers. These copolymers used in this study were produced in homogeneous solution systems by ultrasonic irradiation (1, 3).

On the other hand, mechanochemical block copolymerization in heterogeneous systems of a solid polymer-liquid monomer by ultrasonic irradiation has not been entirely studied. If the block copolymerization in these systems occurs, various kinds of the block copolymer can be synthesized and the decrease in the costs of its manufacture would be expected. In this case, an important matter is a difference in specific acoustic impedances of the solid polymer and liquid monomer. The specific acoustic impedances of the solid polymer and liquid monomer are proportional to the product of those densities and the sound velocities in the polymer and monomer. When that difference shows an enormous value, the ultrasonic waves irradiated in the reaction system cause the total reflection at the solid polymer-liquid monomer interface.

The present paper is concerned with mechanochemical block copolymerization in heterogeneous systems of the solid poly(vinyl chloride)-styrene-sodium dodecyl sulfate aqueous solutions affected by ultrasonic irradiation. In particular, these reaction systems were governed by considering the specific acoustic impedances.

EXPERIMENTAL

Materials

Poly(vinyl chloride) PVC (2B-719, Teijin Co. Ltd.) produced by emulsion polymerization was purified by extraction with hot pure benzene and methyl alcohol for 160 hr. The viscosity-average degree of polymerization was 6,600.

The styrene monomer St was washed successively with sodium thiosulfate solution, water, sodium hydroxide solution, and water. After drying over barium oxide, the monomer was filtered and purified by distillation under reduced pressure in a stream of nitrogen.

Sodium dodecyl sulfate SDS was twice recrystallized from methyl alcohol solution.

The water H_2O was doubly distilled.

Purified benzene and methyl alcohol were used as a polymerization solvent and precipitating agent.

Purified tetrahydrofuran THF and methyl ethyl ketone MEK were used as solvents for the determination of the solution turbidities of polymers.

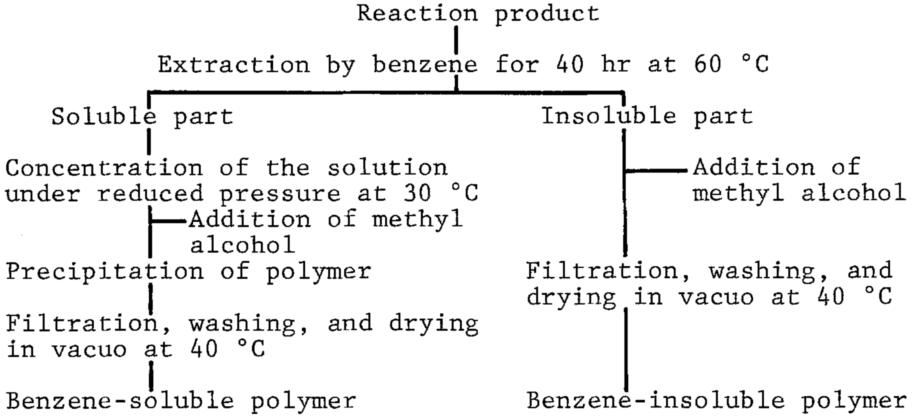
Purified cyclohexanone was used as a solvent for the measurement of the viscosity-average degree of polymerization of PVC.

Apparatus and Procedures

An ultrasonic generator (Model USV-150V, Cho-Onpa Kogyo Co. Ltd.) equipped with a stepped horn of stainless steel on a magnetostrictive nickel vibrator of 25 kHz. The output of this generator had an intensity of 150 watts.

In a typical run for mechanochemical block copolymerization, 2.506 g of the solid PVC, 24.23 g of St, and 54.00 g of SDS aqueous solution (0.500 wt%) were poured into a 300 ml special glass reaction vessel. Ultrasonic irradiation was carried out for 15, 30, 45, 60, and 75 min with the stepped horn in contact with the surface of the solutions under one atmospheric pressure of dry nitrogen at 65 °C. After 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, and

TABLE I. Method of fractional extraction



then the conversion was calculated from the weight of the polymer produced by the copolymerization. The reaction products were fractionated by the procedure shown in Table I. The composition of the block copolymer and homopolymers in the fractionated polymers was determined by turbidimetry (3).

In other experiments, mechanical degradations of PVC were carried out by irradiation of the solid PVC-St-SDS aqueous solutions in the presence of *p*-benzoquinone inhibitor. The viscosity-average degrees of polymerization of PVC at various stages of mechanical degradation were measured by viscometry.

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 benzene-soluble polymer, the solvent and precipitating agent were THF and methyl alcohol. The polymer concentration was 0.015 g/l.

On the other hand, the solvent and precipitating agent for the benzene-insoluble polymer were THF-MEK (50 vol% vs. 50 vol%) and methyl alcohol, respectively. The polymer concentration was 0.67 g/l.

Measurement of the Viscosity-Average Degree of Polymerization

The viscosity-average degrees of polymerization $\overline{Pv}$ of PVC at various stages of mechanical degradation were calculated from the intrinsic viscosities measured in cyclohexanone at 30 °C with the aid of the following relationship (4).

$$\overline{Pv} = (\ \text{Antilog}\ [\eta]\ /\ 0.197\ -\ 1\ )\times 500$$

RESULTS AND DISCUSSION

Mechanochemical Block Copolymerization

An additional effect of the solid PVC on mechanochemical block copolymerization by ultrasonic irradiation is shown in

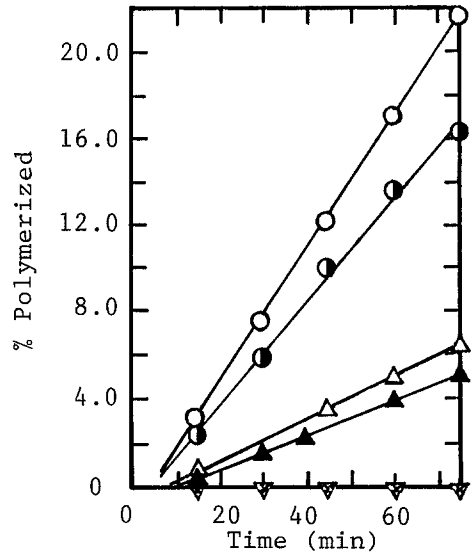


Figure 1. Additional effect of the solid PVC on mechanochemical block copolymerization by ultrasonic irradiation. PVC: (○), 2.993 g; (◑), 2.506 g; (△), 2.311 g; (▲), 1.513 g; (▽), 2.506 g([*p*-Benzoquinone]: 1.15×10^{-2} mol/l); (x), 2.311 g([*p*-Benzoquinone]: 1.15×10^{-2} mol/l). [St]: 2.87 mol/l. [SDS]: 1.16×10^{-2} mol/l. [H_2O]: 36.80 mol/l.

TABLE II. Additional amounts of the solid PVC and the rates of copolymerization *Rp*

PVC (g)	$Rp \times 10^4$ (mol/l sec)
2.993	4.18
2.506	3.27
2.311	1.29
1.513	1.10

Copolymerization condition: [St], 2.87 mol/l; [SDS], 1.16×10^{-2} mol/l; [H_2O], 36.80 mol/l.

Figure 1 and Table II. The rate of copolymerization clearly increases with increasing an additional amount of the solid PVC and this copolymerization is inhibited completely by *p*-benzoquinone. When the solution, in the absence of the solid PVC, was subjected to ultrasonic irradiation, the polymerization of St did not occur under these conditions. These results suggest that mechanochemical block copolymerization of St is initiated by free radicals produced from the PVC particles by ultrasonic waves. In addition, it is considered that the large differences in rates of copolymerization between the reaction systems containing 2.506 g and 2.311 g of the PVC particles are due to the extent of mechanical degrada-

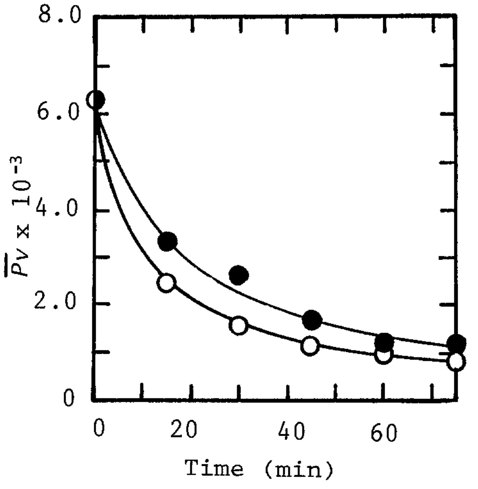


Figure 2. Effect of the additional amounts of the solid PVC on mechanical degradation by ultrasonic irradiation. PVC: (○), 2.506 g; (●), 2.311 g. [*p*-Benzoquinone]: 1.15×10^{-2} mol/l. [St]: 2.87 mol/l. [SDS]: 1.16×10^{-2} mol/l. [H_2O]: 36.80 mol/l.

tion of PVC.

The effect of the additional amounts of the solid PVC on mechanical degradation by ultrasonic irradiation is shown in Figure 2. The values of the viscosity-average degree of polymerization $\overline{Pv}$ of PVC decrease rapidly during the initial 15 min, and then slowly approach the constant ordinate. When 2.506 g of the PVC particles was added in the reaction system, the rate of decrease in $\overline{Pv}$ of the degraded PVC was much faster than that of the reaction system of 2.311 g of PVC. Accordingly, the number of chain scissions of PVC increases greatly at the higher additional amount of the solid PVC. The reason for this phenomenon is thought that the mutual effects of the cavitation and shock waves generated in the reaction system by ultrasonic irradiation were increased with increasing the additional amount of the PVC particles.

The effects of St and SDS concentrations on mechanochemical block copolymerization are shown in Figures 3 and 4. The rates of copolymerization clearly increase with increasing St and SDS concentrations.

The relationships between ln *Rp* and ln [St] in Figure 5 and between ln *Rp* and ln [SDS] in Figure 6 are respectively illustrated. As is obvious from these figures, the linear functions are found in conformity with mechanochemical block

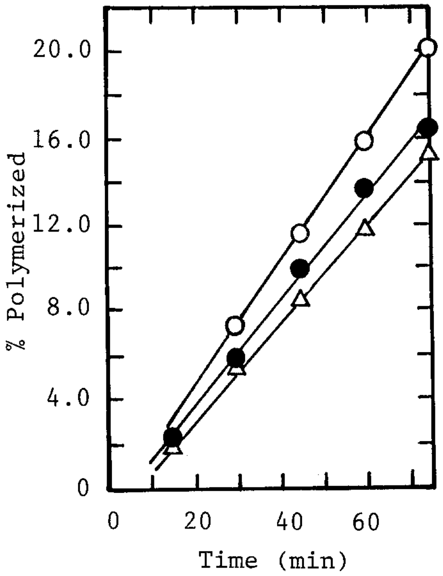


Figure 3. Effect of St concentrations on mechanochemical block copolymerization by ultrasonic irradiation. [St] :(○), 3.02 mol/l; (●), 2.87 mol/l; (△), 2.38 mol/l([Benzene]:0.648 mol/l). PVC:2.506 g. [SDS]: 1.16×10^{-2} mol/l. [H_2O]: 36.80 mol/l.

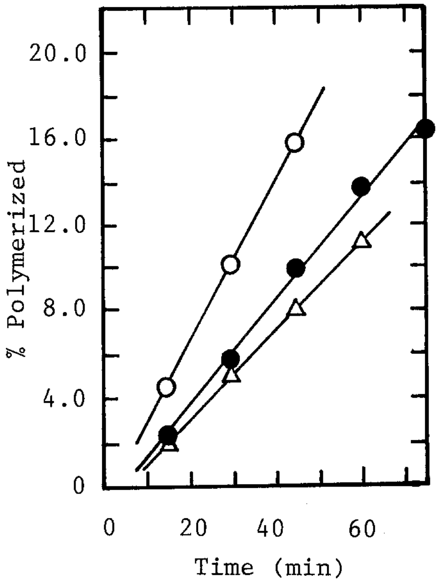


Figure 4. Effect of SDS concentrations on mechanochemical block copolymerization by ultrasonic irradiation. [SDS] :(○), 2.10×10^{-2} mol/l; (●), 1.16×10^{-2} mol/l; (△), 0.690×10^{-2} mol/l. PVC: 2.506 g. [St]: 2.87 mol/l. [H_2O]: 36.80 mol/l.

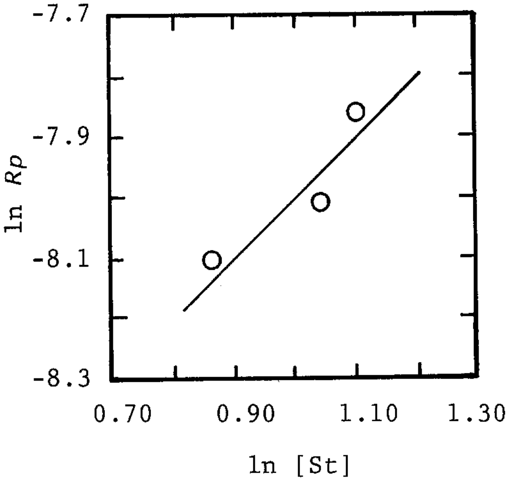


Figure 5. Relationship between ln Rp and ln [St] for mechanochemical block copolymerization of St with the solid PVC. PVC: 2.506 g. [SDS] : 1.16x10^{-2} mol/l. [H_2O] : 36.80 mol/l. [Benzene] :0 ~ 0.648 mol/l.

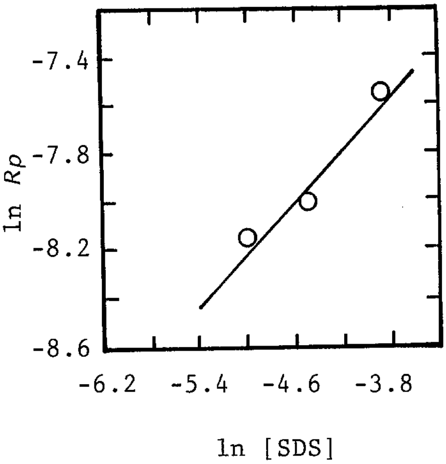


Figure 6. Relationship between ln Rp and ln [SDS] for mechanochemical block copolymerization of St with the solid PVC. PVC: 2.506 g. [St] : 2.87 mol/l. [H_2O] :36.80mol /l.

copolymerization in heterogeneous systems. In addition, the exponents of St and SDS concentrations calculated from the slopes of the straight line in Figures 5 and 6 were 1.0 and 0.54, respectively; these indicate a first-order dependence on [St] and 1/2-order dependence on [SDS].

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

Infrared spectra of the benzene-soluble and the benzene-insoluble polymers in the reaction product were determined by the KBr disk technique with a Japan Spectroscopic FT/IR-3 spectrophotometer. These spectra are shown as an example in Figure 7. The absorption spectra due to the C-Cl bond at 620 cm^{-1} with respect to the benzene-soluble polymer and the phenyl groups at 1950, 1810, 1470, and 1030 cm^{-1} with respect to the benzene-insoluble polymer are respectively recognized. These results indicate that the block copolymer is present as the mixtures in both polymers. In order to obtain more definitive evidence for this matter, the solution turbidities of the fractionated polymers were determined with the turbidimetric titrator.

The compositions of the block copolymer and homopolymers in the reaction products with respect to the irradiation time were obtained from the turbidimetric titration curves. Those results are shown in Figure 8. The weight proportions of PVC decrease with the progress of the block copolymerization, but

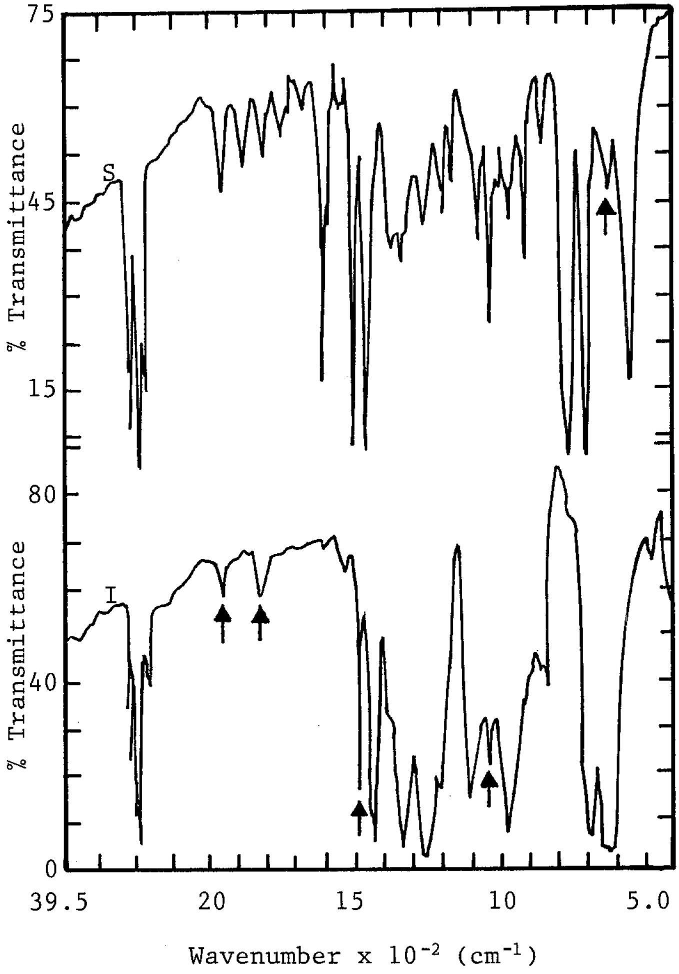
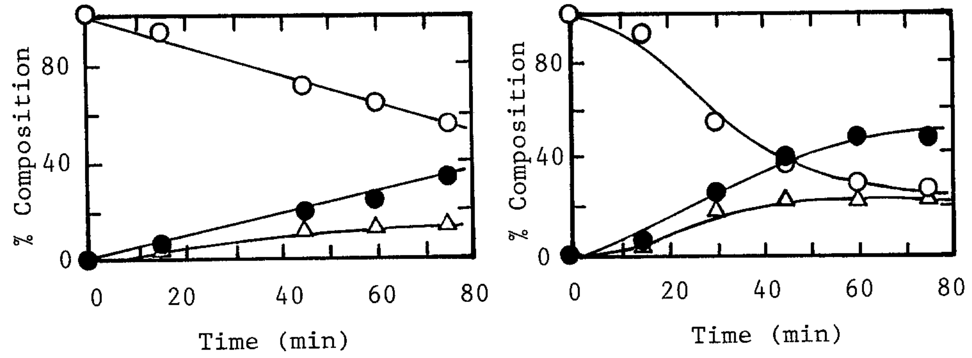


Figure 7. Infrared spectra of the benzene-soluble and the benzene-insoluble polymers. Sample (PVC: 2.506 g. [St]: 2.87 mol /l. [SDS]: $1.16x10^{-2}$ mol/l. [H_2O]: 36.80 mol/l.): polymeric sample, 75 min treatment. (S), benzene-soluble polymer; (I), benzene-insoluble polymer. Phase: suspension in KBr disk.

those of the block copolymer and polystyrene PSt increase. When 2.506 g of the PVC particles was added in the reaction system, the rate of increase in the block copolymer was much faster than that of the reaction system of 2.311 g of PVC and the weight proportion of the block copolymer after 60 min was approximately 50 %. In addition, the formation of PSt is thought to occur since the St segment in the block copolymer underwent mechanical degradation during ultrasonic irradiation



Copolymerization condition: PVC, 2.311 g; [St],2.87 mol/l ; [SDS],1.16×10^{-2} mol/l;[H_2O] , 36.80 mol/l.

Copolymerization condition: PVC, 2.506 g; [St],2.87 mol/l ; [SDS],1.16×10^{-2} mol/l;[H_2O] , 36.80 mol/l.

Figure 8. Changes in the composition of the block copolymers and homopolymers in the reaction products. (○),PVC; (●),block copolymer; (△), PSt.

and the chain transfer reaction to St occurred.

These results suggest that mechanochemical block copolymerizations in heterogeneous systems of other solid polymer-monomer-SDS aqueous solutions effected by ultrasonic irradiation have become feasible.

Acknowledgments

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