Polymer Bulletin 33, 317–323 (1994)

Polymer Bulletin

© Springer-Verlag 1994

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

II. Effect of several forms of suspension polymerized poly(vinyl chloride) particles

Hideki Fujiwara, Takeharu Kikyu, Hajime Nanbu, and Tomohiro Honda

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

Summary

The effect of several forms of suspension polymerized poly(vinyl chloride) particles on mechanochemical block copolymerization in the solid poly(vinyl chloride)-styrene-sodium dodecyl sulfate solutions has been studied by ultrasonic irradiation at 60 ℃. The block copolymerization of styrene was initiated by free radicals produced from the poly(vinyl chloride) particles by ultrasonic waves. The rates of copolymerization increased with increasing the additional amount of the solid poly(vinyl chloride), the porosity, and the average diameter of the grain particles. In particular, the influence of the average diameter was much larger than that of the porosity. When the porosity and the average diameter were increased, the rates of decrease in the viscosity-average degree of polymerization of the degraded poly(vinyl chloride) were much increased. In addition, the changes in the composition of the block copolymer and homopolymers in the reaction products were obtained.

Introduction

When the molding of the rigid poly(vinyl chloride) resin is carried out, the improvement in its moldability is highly demanded. This cause is attributable to that the fluidity of poly(vinyl chloride) is a very poor.

On the other hand, polystyrene has excellent fluidity. The decrease in the costs of the molding of the rigid poly(vinyl chloride) resin has become feasible, provided the characteristics of polystyrene can be endowed with poly(vinyl chloride).

Therefore, it is thought that the defect of the poly(vinyl chloride) resin can be improved by mechanical blending of poly(vinyl chloride) and polystyrene. However, the discontinuous phase of the poly(vinyl chloride) particles and the continuous phase of polystyrene were always present as a mixture in these blending products and the compatibility of both polymers was very poor (1). Accordingly, the coordinating function of vinyl chloride-*b*-styrene copolymers in mechanical blending of poly(vinyl chloride) and polystyrene by open two rolls has been studied in our laboratory. Vinyl chloride-*b*-styrene copolymers were shown to be effective in coordinating both homopolymers (1). These copolymers were produced in homogeneous solution systems by ultrasonic irradiation (1, 2).

On the other hand, if the block copolymerization in heterogeneous systems of the solid poly(vinyl chloride) with styrene occurs, it is thought that the decrease in the costs of its manufacture can be expected and various kinds of the block copolymer can be synthesized. In earlier paper, the study of the block copolymerization in heterogeneous systems of emulsion polymerized poly(vinyl chloride) with styrene by ultrasonic irradiation was shown (3). However, suspension polymerized poly(vinyl chloride) as compared with emulsion polymerized poly(vinyl chloride) is in great request all over the world and the form of the particles differs to a great extent. That is to say, the suspension polymerized poly(vinyl chloride)-grain particles have a diameter of 50 - 200 μm and the outer surface of the grain particles is enveloped by about 1 μm thick shell of polymeric material. The inside of the grain particles contains the primary particles with a diameter of about 1 μm and has an abundance of a porous structure (4, 5).

The present paper is concerned with the effect of several forms of suspension polymerized poly(vinyl chloride) particles on mechanochemical block copolymerization in the solid poly(vinyl chloride)-styrene-sodium dodecyl sulfate solutions by ultrasonic irradiation.

Experimental

Materials

Suspension polymerized poly(vinyl chloride) samples PVC (Kanevinyles, Kanegafuchi Chemical Industry Co., Ltd.) were purified by extraction with hot pure benzene and methyl alcohol for 160 hr. Several forms and viscosity-average degrees of polymerization $\overline{P_v}$ of PVC are summarized in Table I.

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.

TABLE I. Several forms and viscosity-average degrees of polymerization $\overline{P_v}$ of PVC

P V C (Kanevinyl)	Average Particle Diameter D (μm)	Porosity in the PVC-grain Particle P (ml Hg/g PVC)	P/D x 10^2 (ml Hg/g PVC μm)	$\overline{P_v}$
20-1554	120	0.388	0.323	4860
20-1536	125	0.704	0.563	5700
20-1560	151	0.470	0.311	3940
XS-4000	150	0.640	0.427	3880

Purified methyl alcohol and benzene were used as a precipitating agent and a solvent of fractional extraction.
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

The porosities in the PVC-grain particles were determined with a digital readout porosimeter (Model 5-7121B, American Instrument Co., Inc.) under absolute pressure from 20 *psi* to 1000 *psi* at 25 ℃. Those values were indicated by the quantity of mercury inserted in the porosity.
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, 3.000 g of the solid PVC, 22.44 g of St, and 54.76 g of SDS aqueous solution (0.500 wt%) were poured into a 300 ml special glass reaction vessel. Ultrasonic irradiation was carried out for 10, 15, 20, 25, 40, 45, 50, and 60 min with the stepped horn in contact with the surface of the solutions under one atmospheric pressure of dry nitrogen at 60 ℃. 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 ℃, and then the conversion was calculated from the weight of the polymer produced in the copolymerization. The reaction products were fractionated by extraction with benzene for 40 hr at 60 ℃ with a similar manner in the previous paper (3). The composition of the block copolymer and homopolymer in the fractionated polymers was determined by turbidimetry (2, 3).
In other experiments, mechanical degradations of PVC were carried out by the irradiation of the solid PVC-St-SDS solutions in the presence of *p*-benzoquinone inhibitor. The viscosity-average degrees of polymerization $\overline{P}_v$ of PVC at various stages of mechanical degradation were determined 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 ℃. In the case of the benzene-soluble polymer, the solvent and the precipitating agent were THF and methyl alcohol. The polymer concentration was 0.020 g/l. The solvent and the precipitating agent for the benzene-insoluble polymer were THF-MEK (50 vol% vs. 50 vol%) and methyl alcohol, respectively. The polymer concentration was 0.70 g/l.

Determination of the Viscosity-Average Degree of Polymerization

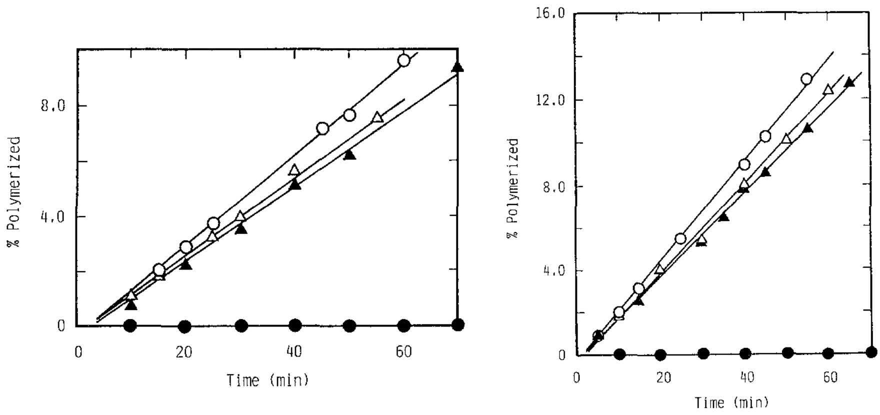
The viscosity-average degrees of polymerization $\overline{P}_v$ of PVC at various stages of mechanical degradation were calculated from the intrinsic viscosities determined in cyclohexanone at 30 ℃ with the aid of the following relationship (6).

$$\overline{P}_v = (\text{Antilog}\,[\eta] \;/\; 0.197 \;-\; 1) \times 500$$

Results and Discussion

The additional effects of the suspension polymerized PVC samples on mechanochemical block copolymerization by ultrasonic irradiation are shown in Figure 1. In either case, the rates of copolymerization R_p clearly increase with increasing the additional amount of the solid PVC and these copolymerizations are 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 in heterogeneous system of the suspension polymerized PVC with St is initiated by free radicals produced from the PVC particles by ultrasonic waves. Further, it is considered that a difference in rates of copolymerization R_p between the reaction systems containing Kane-vinyl 20-1554 and Kane-vinyl 20-1536 is due to the extent of mechanical degradation of the PVC particles and the rate of mechanical degradation in the latter reaction system is probably much faster than that of the former.

The effect of several forms of the PVC particles on mechanochemical block copolymerization is shown in Figure 2 and Table II. When the average diameters of the PVC-grain particles are about the same, the rates of copolymerization R_p clearly increase with increasing the porosities in the grain particles. This result is thought to be due to that the number of grain particles exist in a unit volume of reaction system increases with increasing the porosity, mechanical degradation of the PVC particles is consequently apt to occurred, and the number of free radicals produced from PVC increased.



PVC (Kane-vinyl 20-1554): (○), 3.000 g; (△), 2.300 g; (▲), 2.000 g; (●), 3.000 g ([*p*-Benzoquinone]: 1.15×10^{-2} mol/l).

PVC (Kane-vinyl 20-1536): (○), 3.000 g; (△), 2.500 g; (▲), 2.300 g; (●), 3.000 g ([*p*-Benzoquinone]: 1.15×10^{-2} mol/l).

Figure 1. Additional effect of the suspension polymerized PVC on mechanochemical block copolymerization by ultrasonic irradiation. [St]: 2.63 mol/l. [SDS]: 1.15×10^{-2} mol/l. [H_2O]: 37.13 mol/l.

On the other hand, the rates of copolymerization R_p clearly increase to a great extent with increasing the average diameters of the grain particles. This result is evident that the influence of the average diameter of the grain particle is much larger than that of the porosity at this copolymerization system. 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 to a great extent with increasing the average diameters of the grain particles and mechanical degradation of PVC occurred exceedingly. In addition, mechanical degradation of polymers in homogeneous solution systems by ultrasonic irradiation occurred vigorously in the case of a higher degree of polymerization of polymers and the number of chain scissions was more increased (7). It can be assumed that the rates of copolymerization are increased consequently. However, the rates of copolymerization R_p at this investigation are independent of a difference in the initial degree of polymerization of PVC. Mechanical degradation curves, $\bar{P}_v$ of PVC versus irradiation time, obtained by ultrasonic irradiation are shown in Figure 3. The values of $\bar{P}_v$ of PVC decrease rapidly during the initial step, and then slowly approach the constant ordinate. When the porosity and the average diameter of the grain particles were

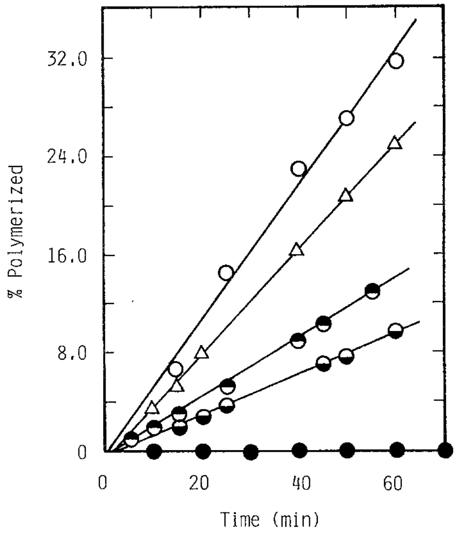


Figure 2. Effect of several forms of the PVC particles on mechanochemical block copolymerization by ultrasonic irradiation. PVC (3.000 g): (○), XS-4000; (△), 20-1560; (◓), 20-1536; (◒), 20-1554; (●), XS-4000 ([p-Benzoquinone]: 1.15×10^{-2} mol/l). [St]: 2.63 mol/l. [SDS]: 1.15×10^{-2} mol/l. [H_2O]: 37.13 mol/l.

TABLE Ⅱ. Several forms of the PVC particles and the rates of copolymerization R_p

P V C (Kane-vinyl)	Average Particle Diameter D (μm)	Porosity P (ml Hg/ g PVC)	P/D x 10^2 (ml Hg/ g PVC μm)	$\bar{P}_v$	R_p x 10^4 (mol/ l sec)
20-1554	120	0.388	0.323	4860	2.30
20-1536	125	0.704	0.563	5700	3.30
20-1560	151	0.470	0.311	3940	6.04
XS-4000	150	0.640	0.427	3880	7.58

Copolymerization condition: PVC, 3.000 g; [St], 2.63 mol/l; [SDS], 1.15×10^{-2} mol/l; [H_2O], 37.13 mol/l.

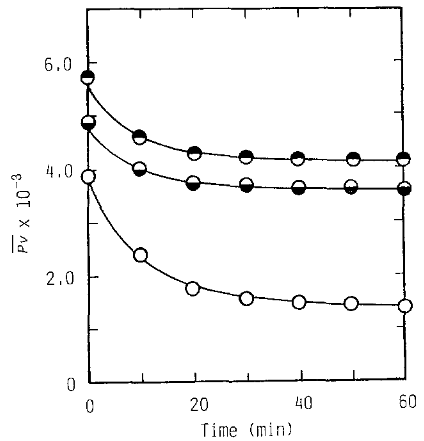


Figure 3. Mechanical degradation of PVC by ultrasonic irradiation. PVC (3.000 g): (◓), 20-1536; (◒), 20-1554; (○), XS-4000. [*p*-Benzoquinone]: 1.15×10^{-2} mol/l. [St]: 2.63 mol/l. [SDS]: 1.15×10^{-2} mol/l. [H_2O]: 37.13 mol/l.

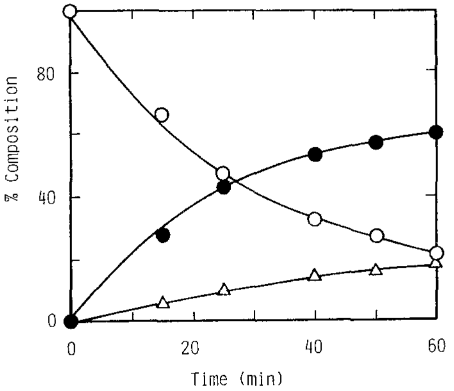
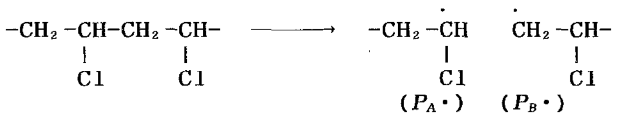


Figure 4. Changes in the composition of the block copolymer and homopolymers in the reaction products. Copolymerization condition: PVC (XS-4000), 3.000 g; [St], 2.63 mol/l; [SDS], 1.15×10^{-2} mol/l; [H_2O], 37.13 mol/l. (○), PVC; (●), block copolymer; (△), PSt.

increased, the rates of decrease in $\overline{P_v}$ of the degraded PVC were much increased. In particular, the influence of the average diameter occurred to a great extent. These results are consistent with the suggested matters from the results of the above copolymerization. Accordingly, it is thought that two end radicals of PVC resulted from ultrasonic degradation are expressed in the following manner and these active ends are responsible for the initiation of mechanochemical block copolymerization.



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

Mechanical degradation

$P_A\cdot$ + St $\longrightarrow$ P_A-St$\cdot$ $\quad$ $P_B\cdot$ + St $\longrightarrow$ P_B-St$\cdot$ Initiation

The changes in the composition of the block copolymer and homopolymers in the reaction products with respect to the irradiation time are shown in Figure 4. The weight proportion of PVC decreases with the progress of the block copolymerization, but those of the block copolymer and polystyrene PSt increase.
In addition, the formation of PSt is thought to occur since the St segment in the block copolymer underwent mechanical degradation during ultrasonic irradiation and the chain transfer reaction to St occurred.

Acknowledgments

We thank Kanegafuchi Chemical Industry Co., Ltd. for the supply of the PVC samples.

References

1. Fujiwara, H. and Goto, K. : *Kobunshi Ronbunshu*, 43, 471 (1986).
2. Fujiwara, H., Kimura, K., Mori, H. and Goto, K. : *Polymer J.*, 13, 927 (1981).
3. Fujiwara, H., Kimura, T., Segi, M., Nakatuka, T., and Nakamura, H. : *Polymer Bull.*, 28, 189 (1992).
4. Allsopp, M. W. : *Pure & Appl. Chem.*, 53, 449 (1981).
5. Tachibana, H. : in *Poly(vinyl chloride), Its Basis and Applications*, Kinki Chemical Soc. (ed.), The Nikkan Kogyo Shimbun Ltd., Tokyo, 1988, p. 214.
6. Sakurada, I. : *Kogyo Kagaku Zasshi*, 47, 133 (1944).
7. Mostafa, M. A. K. : *J. Polym. Sci.*, 33, 295 (1958).

Accepted June 1, 1994 Shi