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Mechanochemical block copolymerization in heterogeneous systems of the solid polyethylene with acrylamide aqueous solutions by ultrasonic irradiation

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Summary

Mechanochemical block copolymerization in heterogeneous systems of the solid polyethylene-acrylamide-sodium dodecyl sulfate aqueous solutions has been studied by ultrasonic irradiation at 30 ℃. An additional effect of the solid polyethylene and the effects of acrylamide, and sodium dodecyl sulfate concentrations on mechanochemical block copolymerization were investigated. The block copolymerization of acrylamide was initiated by free radical produced from the polyethylene particles by ultrasonic waves. The rate of copolymerization R_p increased with increasing additional amount of polyethylene and that value was of the order of 10^{-3} mol/l s. In addition, the R_p was given by $R_p \propto$ [Acrylamide][Sodium dodecyl sulfate].

Introduction

Polyethylene has good pliability and toughness over a wide temperature range and is widely used in all the world. Polyethylene is excellent in moldability and has good resistance to chemical reagents. The electrical properties of polyethylene are outstandingly good and perhaps are situated in next to those of polytetrafluoroethylene.
However, the main disadvantage of polyethylene is very poor in the wettability and the adhesive property. This is because polyethylene does not have polar groups in its molecule. The reforming of the surface of polyethylene can be used at chlorination (1), sulfonation (2), phosphorylation (3), and partial oxidation (4). On the other hand, the reforming of polyethylene by graft copolymerization was carried out using various kinds of monomer by radiation and ozonization techniques (5-9). However, mechanochemical block copolymerization has not been studied.
In earlier paper, the study of mechanochemical block copolymerization in heterogeneous systems of the solid poly(vinyl chloride) with styrene by ultrasonic irradiation was shown (10, 11).

The present paper is concerned with mechanochemical block copolymerization in heterogeneous systems of the solid polyethylene-acrylamide-sodium dodecyl sulfate aqueous solutions affected by ultrasonic irradiation.

Experimental

Materials

Polyethylene PE (Flo-thene M, Sumitomo Seika Chemicals Co., Ltd.) produced by polymerization under high pressure was purified by extraction with hot pure benzene and 2-propanone for 80 hr. The average particle diameter of PE was 275 μm. The acrylamide monomer AA was twice recrystallized from benzene solution. Sodium dodecyl sulfate SDS was twice recrystallized from methyl alcohol solution. The water H_2O was doubly distilled. Purified methyl alcohol was used as a precipitating agent.

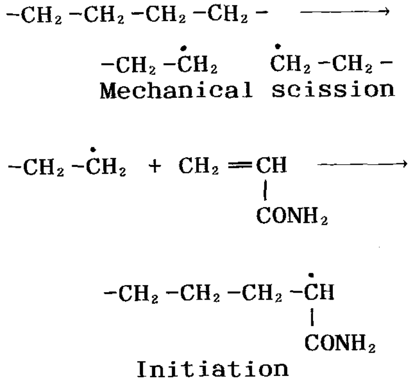
Apparatus and Procedures

An ultrasonic generator (Model USV-200Z-26S, Cho-Onpa Kogyo Co., Ltd.) equipped with an electrostrictive vibrator of 26 kHz was used. The output of this generator had an intensity of 200 watts.

In a typical run for mechanochemical block copolymerization, 1.000 g of the solid PE, 0.500 g of AA, and 45.00 g of SDS aqueous solution (0.500 wt%) were poured into a 200 ml special glass reaction vessel. The center of the bottom of the reaction vessel was contacted on the surface of the vibrator, and then ultrasonic irradiation was carried out for 1, 6, 11, 13, 16, 18, 21, and 26 min under atmospheric pressure of dry nitrogen at 30 ℃. After the reaction, the solution was poured into a large amount of methyl alcohol containing *p*-*t*-butylcatechol 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.

Results and Discussion

An additional effect of the solid PE on mechanochemical copolymerization by ultrasonic irradiation is shown in Figure 1 and Table I. The rate of copolymerization R_p clearly increases with increasing additional amount of PE and that value had the unit of 10^{-3} mol/l s. The large R_p values are because the rate constant k_p, 7.9 x 10^4 l/mol s (12), of propagation reaction of AA is much larger than that of the general vinyl monomers. This copolymerization was inhibited completely by *p*-*t*-butylcatechol inhibitor for free radical polymerization. When the solution, in the absence of the solid PE, was subjected to ultrasonic irradiation, the polymerization of AA did not occur under these conditions. These results suggest that mechanochemical block copolymerization in heterogeneous system of the solid PE with AA is initiated by free radicals produced from the PE particles by ultrasonic vibration. In addition, it is considered that the differences in rate of copolymerization from the reac-



$$-CH_2-CH_2-CH_2-CH_2- \longrightarrow -CH_2-\dot{C}H_2 \quad \dot{C}H_2-CH_2-$$

Mechanical scission

$$-CH_2-\dot{C}H_2 + CH_2{=}\underset{\displaystyle CONH_2}{CH} \longrightarrow -CH_2-CH_2-CH_2-\underset{\displaystyle CONH_2}{\dot{C}H}$$

Initiation

tion systems containing 0.400 g to 1.000 g of the PE particles are due to the number of chain scissions of PE.

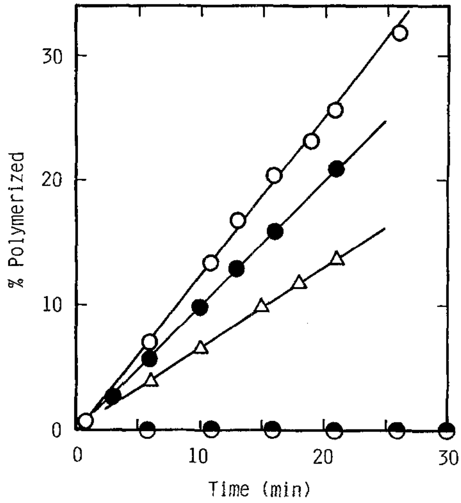


Figure 1. Additional effect of the solid PE on mechanochemical block copolymerization by ultrasonic irradiation. PE: (○), 1.000 g; (●), 0.600 g; (△), 0.400 g; (◓), 1.000 g ([*p*-*t*-Butylcatechol]: 1.34×10^{-3} mol/l). [AA]: 0.1563 mol/l. [SDS]: 1.73×10^{-2} mol/l. [H_2O]: 55.3 mol/l.

TABLE I. Additional amounts of the solid PE and the rates of copolymerization R_p

PE (g)	$R_p \times 10^3$ (mol/l s)
1.000	3.28
0.600	2.80
0.400	1.87

Copolymerization condition: [AA], 0.1563 mol/l; [SDS], 1.73×10^{-2} mol/l; [H_2O], 55.3 mol/l.

The effect of AA concentration on mechanochemical block copolymerization is shown in Figure 2. The rate of copolymerization clearly increases with increasing AA concentration. For the purpose of determination of the reaction order, the relationship between ln R_p and ln [AA] is illustrated graphically in Figure 3. As is obvious from this figure, a plot of ln R_p vs. ln [AA] gave a straight line. The exponent of AA concentration calculated from the slope of the straight line in Figure 3 is 1.0. This indicates a first order dependence on [AA].

The effect of SDS concentration on mechanochemical block copolymerization is shown in Figure 4. The rate of copolymerization increases with increasing SDS concentration. This is evident that the influence of the number of micelle in the reaction system is of importance.

The relationship between ln R_p and ln [SDS] is illustrated graphically in Figure 5. A plot of ln R_p vs. ln [SDS] gave a straight line and the reaction order is found to be 1.0. These results indicate that the rate of copolymerization R_p

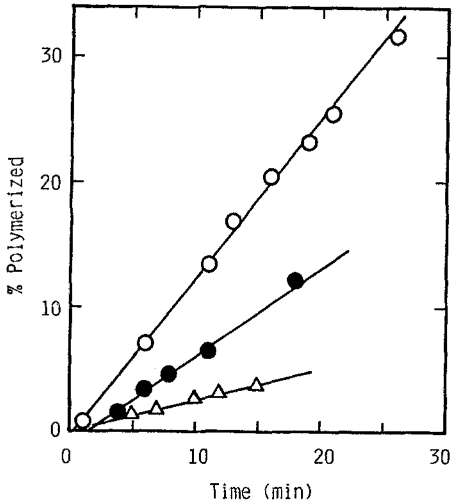


Figure 2. Effect of AA concentration on mechanochemical block copolymerization by ultrasonic irradiation. [AA]: (○), 0.1563 mol/l; (●), 0.0938 mol/l; (△), 0.0626 mol/l. PE: 1.000 g. [SDS]: 1.73x10^{-2} mol/l. [H_2O]: 55.3 mol/l.

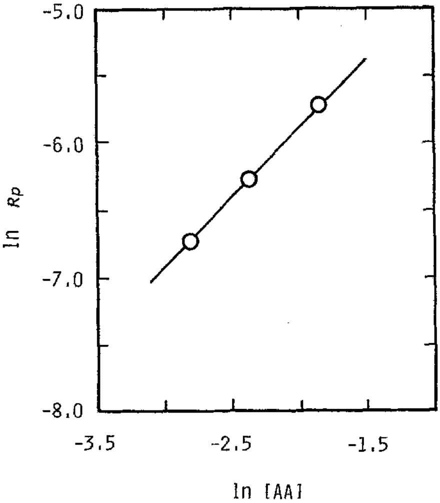


Figure 3. Relationship between ln R_p and ln [AA]. PE: 1.000 g. [SDS]: 1.73x10^{-2} mol/l. [H_2O]: 55.3 mol/l.

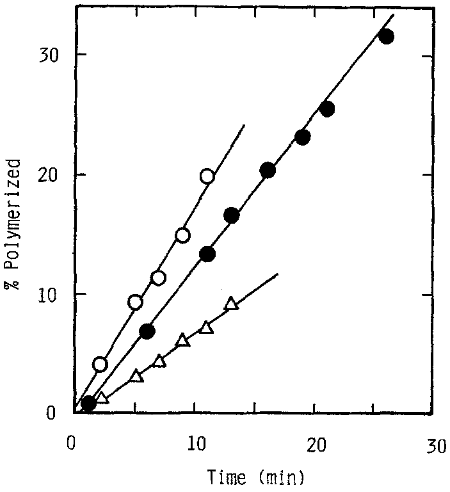


Figure 4. Effect of SDS concentration on mechanochemical block copolymerization by ultrasonic irradiation. [SDS]: (○), 2.08x10^{-2} mol/l; (●), 1.73x10^{-2} mol/l; (△), 1.04x10^{-2} mol/l. PE: 1.000 g. [AA]: 0.1563 mol/l. [H_2O]: 55.3 mol/l.

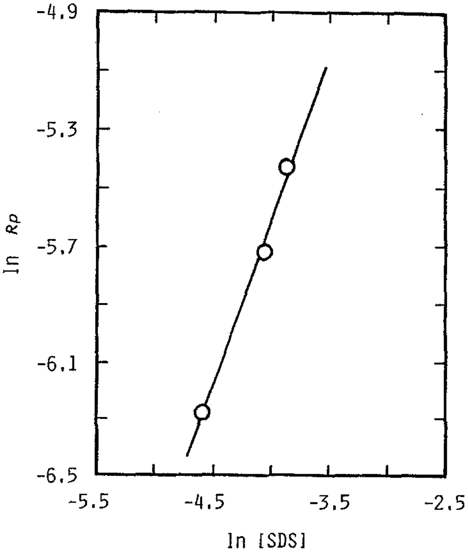


Figure 5. Relationship between ln R_p and ln [SDS]. PE: 1.000 g. [AA]: 0.1563 mol/l. [H_2O]: 55.3 mol/l.

is given by $R_p \propto$ [AA][SDS].

The reaction products were fractionated by extraction with distilled water for 40 hr at 70 ℃. Infrared spectra of the water-insoluble and the water-soluble 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 examples in Figure 6. The absorption spectra due to the $-CONH_2$ groups at 3450 and 1650 cm^{-1} with respect to the water-insoluble polymer (I) and the $-CH_2-$ groups at 2930, 2850, 1470, and 730 cm^{-1} with respect to the water-soluble polymer (S) are respectively recognized. These results indicate that the block copolymers are present as the mixtures together with an unreacted PE in the water-insoluble and the homopolymer of AA in the water-soluble

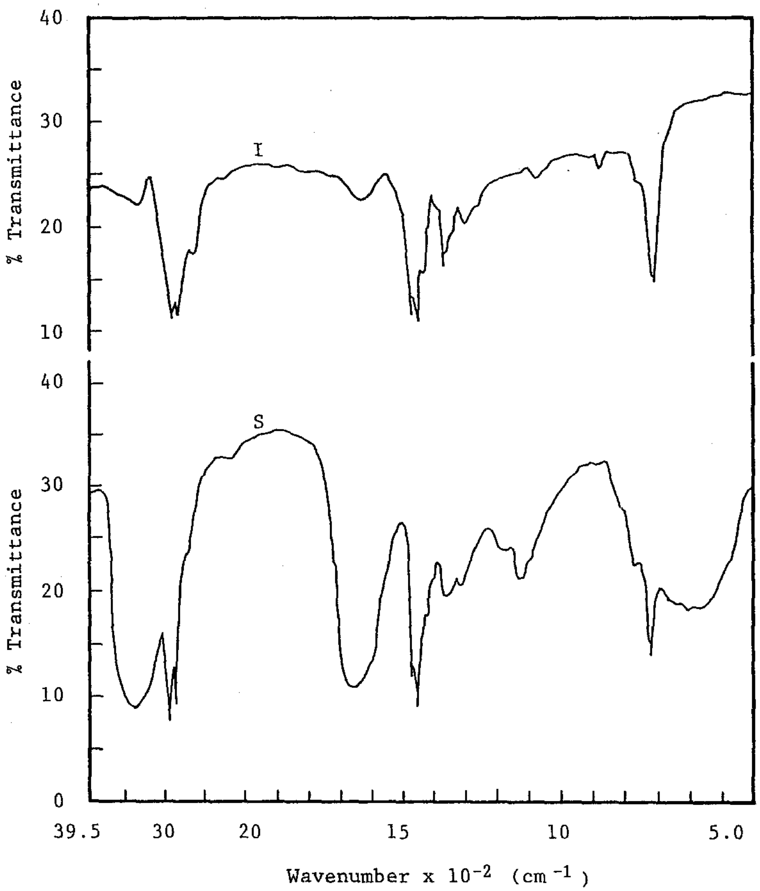


Figure 6. Infrared spectra of the water-insoluble and the water-soluble polymers. Sample (PE: 1.000 g. [AA]: 0.1563 mol/l. [SDS]: 1.73×10^{-2} mol/l. [H_2O]: 55.3 mol/l.): polymeric sample, 26 min treatment. (I), water-insoluble polymer (77.6 wt%); (S), water-soluble polymer (22.4 wt%). Phase: suspension in KBr disk.

polymers. In addition, the formation of polyacrylamide PAA is thought to occur since the AA segment in the block copolymer underwent mechanical scission during ultrasonic irradiation and the chain transfer reaction to AA occurred.

Acknowledgments

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