Polymer Bulletin 25, 571–574 (1991)

Polymer Bulletin

Mechanochemical polymerization in mixtures of diallyl terephthalate and distilled water 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

Mechanochemical polymerization in systems of diallyl terephthalate-distilled water has been studied by ultrasonic irradiation at 90 ℃. An additional effect of distilled water on mechanochemical polymerization of diallyl terephthalate was investigated. When a 1.2 wt % distilled water solution, the conversion of poly(diallyl terephthalate) was the greatest and the initial rate of the polymerization R_p was 1.3×10^{-5} mol/l sec. This polymerization proceeded by a radical mechanism and the primary radicals produced from water molecules by ultrasonic waves. In addition, changes in the iodine value and the weight-average molecular weight of the resulting polymers were proved.

INTRODUCTION

Poly(diallyl terephthalate) has excellent properties such as dimensional stability and rigidity under heat, impact, heat, and moisture resistances and excellent electrical properties (1, 2). However, the cost of its production is relatively high because it is due to the use of organic peroxides or azo compounds (1) and organic solvents (1) at high temperatures. Accordingly, we have tried a decrease in the cost of the production by the use of the mechanochemical method.

Mechanochemical polymerizations of polystyrene-styrene (3), polystyrene-methyl methacrylate (4), polybutadiene-styrene (5), poly(vinyl chloride)-styrene (6), poly(vinyl chloride)-methyl methacrylate (7), poly(vinyl alcohol)-methyl methacrylate (8), aluminum acetylacetonate-styrene (9), and aluminum acetylacetonate-styrene-methyl methacrylate (10) by ultrasonic irradiation have been studied in our laboratory.

On the other hand, an investigation has shown that the ultrasonic waves decompose water molecules into the hydrogen and hydroxyl free radicals (11).

In the present paper, we deal with mechanochemical polymerization in systems of diallyl terephthalate-distilled water effected by ultrasonic irradiation.

EXPERIMENTAL

Materials

The diallyl terephthalate monomer DATP (Dapren, Daiso Co. Ltd.) was purified by distillation under reduced pressure in a stream of nitrogen.

Distilled water and purified methanol were used as an initiator of the polymerization and the precipitating agent.

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 210 watts.

In a typical run, 83.6 g of DATP and 1.0 g (1.2 wt %) of distilled water were poured into a 130 ml special glass reaction vessel. Ultrasonic irradiation was carried out for 30, 60, 120, 150, 180, and 240 min with the stepped horn in contact with the surface of the DATP-distilled water mixtures under one atmospheric pressure of dry nitrogen at 90 ℃. After reaction, the solution was poured into a large amount of methanol containing *p*-benzoquinone inhibitor. The precipitated polymer was filtered, washed, and dried in vacuo at 45 ℃, and then the conversion was calculated from the weight of the polymer produced by the polymerization.

The iodine value and the weight-average molecular weight of the resulting polymers were determined by the Wijs and gel permeation chromatography methods.

Determination of the iodine value

Poly(diallyl terephthalate) PDATP is characterized by having a degree of unsaturation that expressed as the iodine value IV measured by the Wijs method. The IV is derived mainly from the double bonds of the residual allyl groups in PDATP.

PDATP was precisely weighed in the range of 0.50 to 0.60 g and put in a 300 ml Erlenmeyer flask provided with a ground stopper. About 30 ml of chloroform was added to dissolve the polymer completely. Twenty ml of the Wijs reagent and 10 ml of a 25 % glacial acetic acid solution of mercuric acetate were accurately added and the mixture was allowed to stand in a dark place for 20 min to complete the reaction. Then, 5 ml of a 20 % aqueous KI solution was added and the mixture was titrated with a 0.1 *N*-$Na_2S_2O_3$ standard solution by the use of a 1 % aqueous starch solution as an indicator. At the time of titration, the flask was vigorously shaken. A blank test was also carried out.

Determination of the weight-average molecular weight

The weight-average molecular weight $\overline{M_w}$ of PDATP was determined by gel permeation chromatography (Model 150C GPC, Waters Co. Ltd.) at 35 ℃. Two 10^2 Å Waters micro column series and one each of 5×10^2 Å, 10^3 Å, 10^4 Å, and 10^5 Å were connected to series in this order. Tetrahydrofuran was used as a solvent and a flow rate was 2.0 ml/min.

RESULTS AND DISCUSSION

An additional effect of distilled water on mechanochemical polymerization of DATP by ultrasonic irradiation is shown in Figure 1. When a 1.2 wt % distilled water solution, the conversion of PDATP was the greatest. This is because this

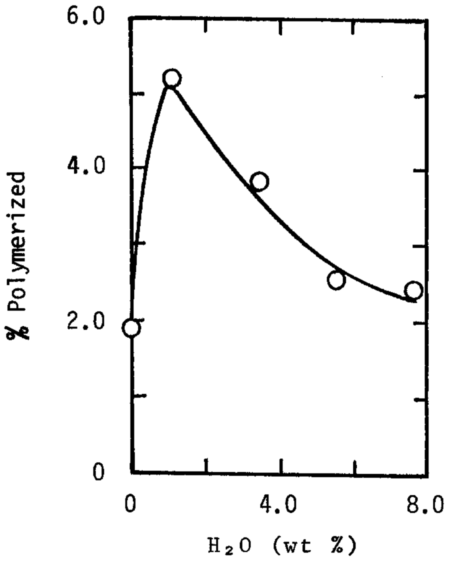

Figure 1. Additional effect of distilled water on mechanochemical polymerization of DATP by ultrasonic irradiation. DATP: 83.6 g. Irradiation time: 180 min.

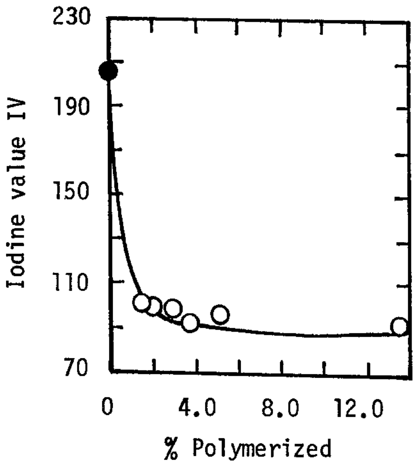

Figure 3. Relationship between the conversion and the IV of PDATP on mechanochemical polymerization. Polymerization conditions: DATP, 83.6 g; distilled water, 1.0 g (1.2 wt %).

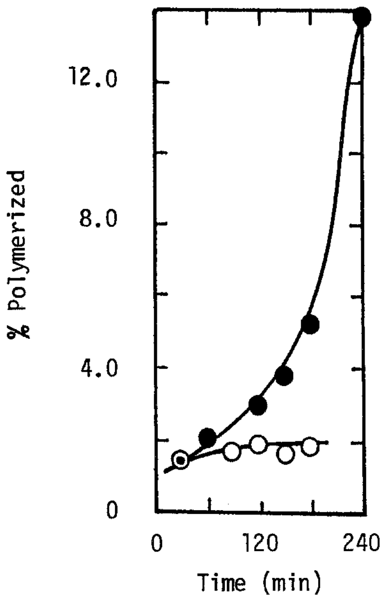

Figure 2. Relationship between the irradiation time and the conversion of PDATP on mechanochemical polymerization. DATP: 83.6 g. Distilled water: (○), 0 g; (●), 1.0 g (1.2 wt %).

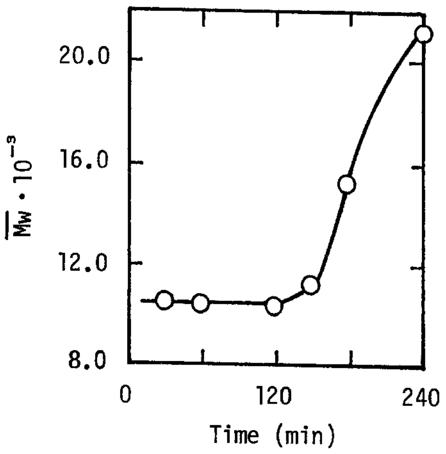

Figure 4. Change in the $\overline{M_w}$ of the resulting polymer at various stages of mechanochemical polymerization. Polymerization conditions: DATP, 83.6 g; distilled water, 1.0 g (1.2 wt %).

reaction system always was homogeneous solution. Inhomogeneities in the systems increased with increasing an additional amount of distilled water and the produced polymer is particularly apt to precipitate in this reaction system. This polymerization was inhibited completely by *p*-benzoquinone. When the solution, in the absence of ultrasonic irradiation, was subjected to heat, the polymerization of DATP did not occur.

The relationship between the irradiation time of ultrasonic waves and the conversion of PDATP on mechanochemical polymerization is shown in Figure 2. In the absence of distilled water, the polymerization of DATP proceeds hardly. However, the rate of polymerization in a system of DATP-distilled water solution increases with increasing irradiation time. The initial rate of mechanochemical polymerization R_p in this reaction system was 1.3×10^{-5} mol/l sec.

These results suggest that an increase in the rate of polymerization in a system of DATP-distilled water solution is due to the hydrogen and hydroxyl free radicals produced from water molecules by ultrasonic waves.

The relationship between the conversion and the IV of PDATP on mechanochemical polymerization is shown in Figure 3. The IV of DATP was 206. The curve decreases rapidly during the initial 1.5 wt %, and then slowly approaches a constant ordinate. This result suggests that a part of the allyl groups resides in the resulting polymer and the reaction of those groups proceeds slowly with increasing yield of PDATP.

Change in the $\overline{M_w}$ of the resulting polymer at various stages of mechanochemical polymerization is shown in Figure 4. The value of the $\overline{M_w}$ was initially about 11,000, but increased with irradiation time after polymerization for 120 min. This result indicates that the reaction of the residual allyl groups in the resulting PDATP proceeded as described previously.

Acknowledgments

We thank Dr. M. Tanaka and Dr. M. Osuka of Daiso Co. Ltd. for supporting this work.

REFERENCES

1. Tanaka, M., Osuka, M., Kuri, T. and Takakuwa, S. (Daiso Co. Ltd.): *U. S. Pat.* 4,518,764 (1985)
2. Tanaka, M., Kuri, T. and Osuka, M.: *Thermosetting Resin* **7**, 14 (1986)
3. Fujiwara, H., Okazaki, K. and Goto, K.: *J. Polym. Sci., Polym. Phys. Ed.* **13**, 953 (1975)
4. Fujiwara, H. and Goto, K., *et al.*: *Kobunshi Ronbunshu* **33**, 183 (1976)
5. Fujiwara, H. and Goto, K., *et al.*: *Nippon Gomu Kyokaishi* **52**, 247 (1979)
6. Fujiwara, H. and Goto, K., *et al.*: *Polym. J.* **13**, 927 (1981)
7. Fujiwara, H. and Goto, K.: *Polym. Bull.* **23**, 27 (1990)
8. Fujiwara, H. and Goto, K.: *Kobunshi Ronbunshu* **41**, 133 (1984)
9. Fujiwara, H., Inoue, I. and Goto, K.: *Kobunshi Ronbunshu* **37**, 741 (1980)
10. Fujiwara, H. and Goto, K.: *Kobunshi Ronbunshu* **39**, 481 (1982)
11. Edelmann, K.: *J. Polym. Sci.* **29**, 531 (1958)

Accepted January 26, 1991 S