

High Pressure Copolymerization Reaction of Fumaronitrile with *trans*-Stilbene

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Synopsis

Radical copolymerization reaction of fumaronitrile with *trans*-stilbene was investigated under high pressure up to 4000 kg/cm². The yield and the fumaronitrile content of copolymer increased with pressure, but its molecular weight is independent of pressure. The obtained copolymer is yellowish substance.

1. Introduction

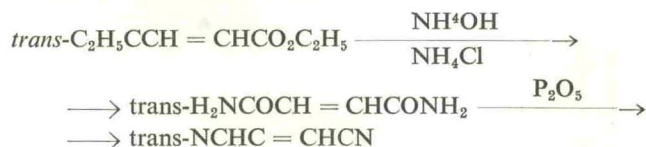
Quantitative treatments of radical copolymerizations have generally assumed that the reactivity of a growing free radical is determined solely by its terminal monomer unit. However, the reactivity of a growing chain is influenced by the nature of other-than-terminal units in some copolymerization systems and these systems have been called copolymerization possessing penultimate effect. The copolymerization system involving fumaronitrile is the example which gave evidence of the effect of penultimate units on adding monomer¹⁾. This effect is attributed to polar and steric causes which lead to repulsion between chains rich in fumaronitrile and the adding fumaronitrile monomer.

It was suggested in our previous papers²⁾ that high pressure is presumed to be effective for eliminating the penultimate effect on the copolymerization. *Trans*-Stilbene is known to be difficult to homopolymerize by radical mechanism because of its steric hindrance³⁾. Since fumaronitrile also does not homopolymerize, the reactions with *trans*-stilbene and fumaronitrile are expected to proceed 1:1 alternating copolymerization. Accordingly, penultimate monomer is always fumaronitrile on this copolymerization, and then the reaction might be accelerated with pressure. From this standpoint, copolymerization reaction with fumaronitrile and *trans*-stilbene were carried out under high pressure.

2. Experimental

Benzoylperoxide (abbreviated as BPO below) used as a initiator and acetone and *n*-hexane used as solvent were purified by the usual method.

Fumaronitrile was synthesized from diethylfumarate and recrystallized from benzene-petroleum ether (M.P. 96 - 97°C)⁴⁾. The synthetic route is as follows.

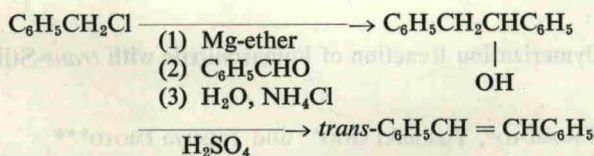


trans-Stilbene was synthesized from benzylchloride and benzaldehyde and recrystallized from methanol (M.P. 124°C). The synthetic route is as follows.

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The mixture containing 1.1×10^{-2} mole fumaronitrile, 1.1×10^{-2} mole *trans*-stilbene, 2.2×10^{-4} mole BPO, 2.1×10^{-4} mole acetone and 1.7×10^{-1} mole benzene were reacted at 90°C temperature under up to 4000 kg/cm^2 pressure. The copolymer mixture thus obtained was precipitated into a large amount of *n*-hexane as precipitant, dried completely at room temperature and its copolymerization yield determined. The copolymer purified by acetone-methanol reprecipitation method. The molecular weight by boiling point rising method, elementary analysis and the infrared (IR) spectrum were determined.

3. Results and Discussion

The obtained copolymer was yellowish substance and the IR spectra of the copolymer are shown in Fig. 1. On the basis of these spectra, it seemed reasonable to assume that the fumaronitrile copoly-

merizes as the shape of $\begin{array}{c} \text{CN} \\ | \\ -\text{C}-\text{C}- \\ | \\ \text{CN} \end{array}$ and does not copolymerize by cyano bond since cyano group absorption is strongly recognized at 2240 cm^{-1} . The peak of the spectra at 1700 cm^{-1} is carbonyl band from BPO and the absorption at 1603 , 759 and 700 cm^{-1} show phenyl group from the *trans*-stilbene.

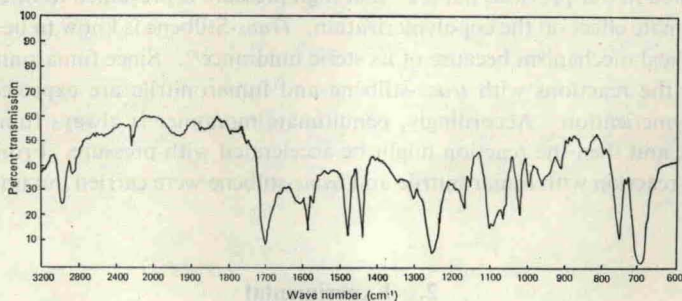


Fig. 1 IR spectra of copolymer

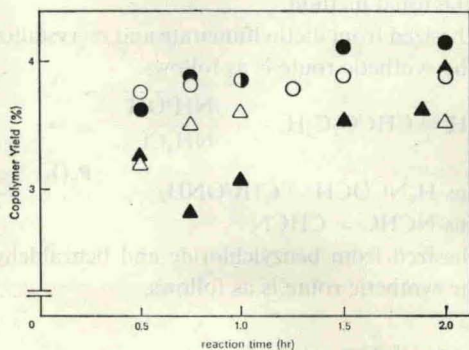


Fig. 2 Effect of pressure on copolymerization yield.

▲ : 100, △ : 2000, ● : 3000, ○ : 4000 kg/cm^2

The variations of copolymer yield with polymerization time at 90°C are shown in Fig. 2. The rate of copolymerization was accelerated by pressure, however yield itself was considerably small and the effect of polymerization time was not so marked as for the effect of pressure.

The result of elementary analysis and molecular weight of copolymer were shown in Table 1. The copolymers were all of very low molecular weight and the molecular weight were not affected by pressure. These facts suggest that this copolymerization system is different from the customary copolymerization using radical initiator. However, there is no definite evidence that this is due to the different copolymerization mechanism.

Table 1 Elementary analysis and molecular weight of copolymer

pressure (kg/cm ²)	elementary analysis (%)				molecular weight
	C	H	O	N	
100	81.97	5.47	4.35	8.21	2000
2000	81.99	5.44	3.99	8.53	2500
3000	81.57	5.47	4.24	8.72	1600
4000	81.28	5.47	4.52	8.73	2000

As shown in Table 1, the content of nitrogen in the copolymer increased with pressure. These facts indicate that the fumaronitrile rich copolymer is easy to form under high pressure because its penultimate effect tends to disappear with pressure and are in agreement with our previous conclusion that high pressure is presumed to be effective for eliminating the penultimate effect on the copolymerization.

Reference

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