Photopolymerization of Vinyl Monomers Using Benzophenone-Tetrahydrofuran Initiation System and Aldehydes at Low Temperatures

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Synopsis

The photopolymerizations of vinyl trifluoroacetate (VTFAc), vinyl acetate (VAc), and methyl methacrylate (MMA) using the initiation system benzophenone–tetrahydrofuran were studied at low temperatures. At −78°C the rate of polymerization of VTFAc was higher than that of VAc, while MMA, which was solidified, did not polymerize. After melting the irradiated solid mixture the polymerization occurred at 4°C. The photoinduced polymerization of VTFAc occurred in the presence of butylaldehyde or isobutylaldehyde at −70°C. The degrees of polymerization and syndiotacticities of the polymers prepared were investigated.

INTRODUCTION

The authors have reported the properties of syndiotacticity-rich poly(vinyl alcohol)s prepared from the polymers obtained through the radical polymerization of vinyl trifluoroacetate (VTFAc).[1-4] The syndiotacticity of the polymers obtained through the bulk polymerization at 60°C is ca. 55% in syndiotactic diads (s-diad). When more syndiotacticity-rich polymers are required, as is well known, the polymerization is conducted at lower temperatures. The rate of polymerization, however, decreases with decreasing polymerization temperature. In this laboratory, the polymerization of VTFAc at 0–78°C has been conducted through the photoinduced decomposition of 2,2'-azobis(2,4-dimethylvaleronitrile) (AZVN). The rate of polymerization of VTFAc containing 1% of AZVN at −78°C is very slow, and no more AZVN is employed due to limited solubility. Benzophenone (BP)/tetrahydrofuran (THF) is reported to initiate the photopolymerization.[5] This initiation system was applied for the polymerization of VTFAc. The polymerization with this system was also applied for vinyl acetate (VAc) and methylmethacrylate (MMA) for comparison. In addition, the photoinduced polymerization of VTFAc in the presence of aldehydes was conducted.

EXPERIMENTAL

Reagents

VTFAc was synthesized by the reaction of trifluoroacetic acid and acetylene in liquid phase according to the method reported by Haas et al.[6] The

monomer having a boiling range of 38.5–39.0°C was used. VAc was purified as follows: First it was distilled under reduced pressure in the presence of hydroquinone, then the monomer was partially polymerized at 60°C for 1 h in the presence of 2,2'-azobisisobutylnitrile, and distilled in a stream of nitrogen. The monomer having a boiling range of 71.5–72.5°C was used. MMA was twice distilled under reduced pressure in the presence of hydroquinone. The monomer having a boiling range of 42.0–43.0°C (90 mm Hg) was used.

Commercial BP, AZVN, and THF were used without further purification. Butylaldehyde (BA) and isobutylaldehyde (IBA) were distilled three times. Reagents described above were purchased from Wako Chemicals (Japan).

Polymerization

All the polymerizations were conducted in sealed Pyrex glass tubes of 1 cm i.d. In the cases of VTFAc and VAc, oxygen was purged by several flashings of nitrogen gas at −78°C, and in the case of MMA with a freeze–thaw method (three times). The light source was a 400 W Hg lamp. After irradiation, poly(vinyl trifluoroacetate) (PVTFAc) and poly(methylmethacrylate) (PMMA) were separated from the reaction mixture by dilution with acetone followed by precipitation in petroleum benzine, and poly(vinyl acetate) (PVAc) was separated from the reaction mixture without dilution.

Characterization

The viscosity average degree of polymerization (DPv) of PVTFAc was determined by viscometry after converting to PVAc whereas DPv of PVAc and PMMA was determined without conversion. The modified Sakurada–Houwink–Mark equations in which molecular weights are replaced by DPvs were used.

$$[\eta] = 8.91 \times 10^{-3} \, DPv^{0.62} (dLg^{-1}, 30°C, benzene) \, (PVAc)^{7}$$

$$[\eta] = 1.72 \times 10^{-3} \, DPv^{0.62} (dLg^{-1}, 30°C, benzene) \, (PMMA)^{8}$$

PVTFAc was converted to PVAc after acetylation with acetic anhydride/pyridine of PVA prepared by the ammonolysis with 2,2'-diamino diethylamine. The syndiotacticities were estimated from the infrared spectrum of PVA film using the following equation[9]:

$$s\text{-diad \%} = 92.4 \times (D_{916}/D_{849})^{0.43}$$

where D_{916} and D_{849} are the absorbances at 916 and 849 cm^{-1}, respectively. The polymers derived from VAc were converted to PVA with methanol/sodium hydroxide.[10]

RESULTS

Figure 1 shows the time–conversion curve for VTFAc at −78°C using the initiation system BP–THF. After 8.5 h about 35% of VTFAc was converted to PVTFAc.
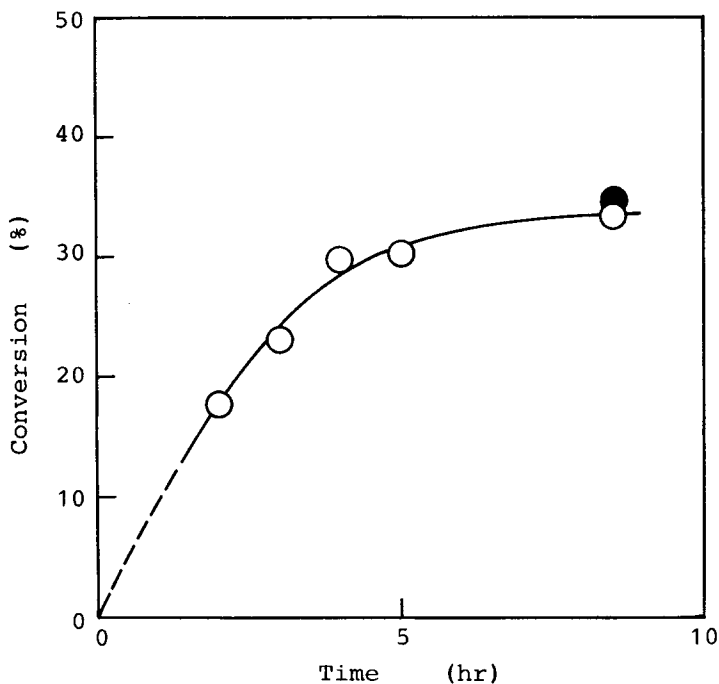
Fig. 1. Time–conversion curve for VTFAc–BP–THF at −78°C. The distance between the light source and polymerization tube = 6 cm, total volume = 5.45 mL, and THF = 4.6 vol %. (○)BP = 0.077% (5.0 × 10⁻³ mol/L); (●) BP = 0.046% (3.0 × 10⁻³ mol/L).
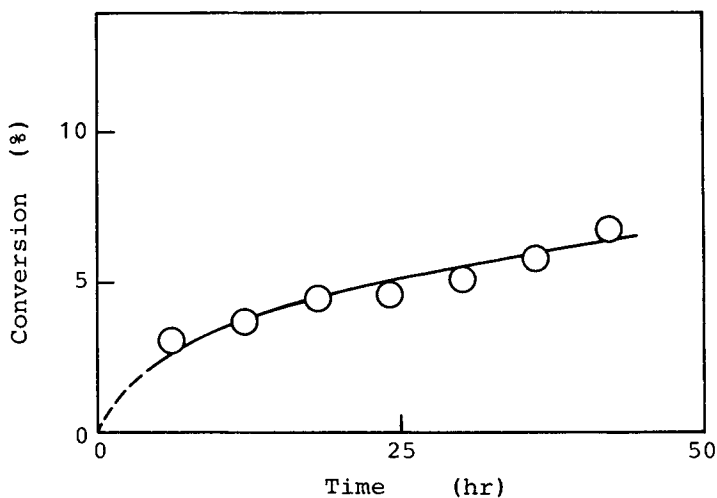

Fig. 2. Time–conversion curve for VAc–BP–THF at −78°C. The distance between the light source and polymerization tube = 6 cm, total volume = 5.45 mL, THF = 4.6 vol %, and BP = 0.059% (3.0 × 10⁻³ mol/L).

TABLE I
Viscosity Average Degree of Polymerization (DPv) and Syndiotacticity ($s\%$) of the
Poiymers Prepared by the Photoinduced Polymerization of VTFAc and VAc Using BP–THF

Sample no.	Monomer	BP (10^3 mol/L)	THF (vol %)	Polym. time (h)	Conversion (%)	DPv	$s\%$
1	VTFAc	5.0	4.6	4	30	1830	64
2	VTFAc	3.0	4.6	23	57	1300	64
3	VAc	3.0	4.6	42	6.8	740	—
4	VAc	3.1	1.9	43	6.8	550	50

TABLE II
Polymerization of MMA Using BP–THF[a]

Radiation time at $-78°C$ (h)	Standing time at $4°C$ (h)	Conversion (%)	DPv
18	0	0.92	—
18	48	6.5	12,300
18	72	15	13,700
18	90	20	11,500
12	0	0.85	—
12	82	17	21,300
0	164	0	—

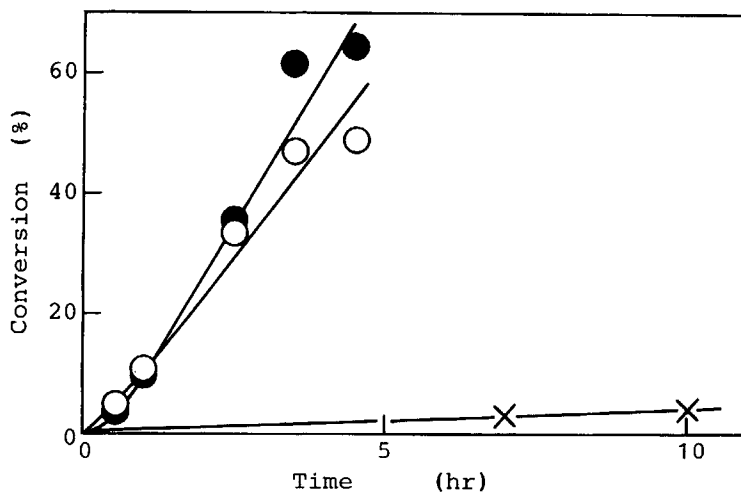[a] BP: 3.0×10^{-3} mol/L (0.059%), THF 4.6 vol %, total volume 5.45 mL.

Fig. 3. Time–conversion curves for VTFAc–aldehyde–AZVN at $-70°C$. The distance between the light source and polymerization tube = 12 cm: (○) BA 20 vol %, AZVN 0.43%, total volume 5.20 mL; (●) IBA 20 vol %, AZVN 0.43%, total volume 5.20 mL; (×) AZVN 0.50%, total volume 4.2 mL.

Figure 2 shows the time–conversion curve for VAc with same conditions. The rate of polymerization of VAc is considerably lower than that of VTFAc.

Table I shows the DPvs and syndiotacticities of PVTFAcs and PVACs prepared using the initiation system. The DPvs of PVTFAcs were in the range between 1000 and 2000 whereas those of PVAc were lower than 1000.

Table II shows the polymerization of MMA using the same initiation system. Since the melting point of MMA is $-48.3°C$, the monomer–BP–THF mixture solidified at $-78°C$. The polymerization of MMA hardly occurred at $-78°C$. When solidified mixtures were, however, melted and allowed to stand at ca. 4°C in darkness in a freezer, the viscosity of the mixtures increased slowly with time. The polymerization of MMA did not occur for the mixture without irradiation even after standing for 164 h at ca. 4°C. The DPv was in the range of 1.2×10^4–2.1×10^4.

Figure 3 shows the time–conversion curves for VTFAc at $-70°C$ in the presence of BA or IBA and AZVN. Enhanced polymerization rates due to the aldehydes were observed. After 4 h irradiation in the presence of BA, 61.4% of VTFAc was converted to PVTFAc which had DPv of 85.

DISCUSSION

The initiation system BP–THF is useful to prepare PVTFAc at $-78°C$. The rate of polymerization and the DPv are satisfactory. The rate of polymerization of VAc at $-78°C$ is considerably lower than that of VTFAc. The rate of polymerization (R_p) in radical polymerization is represented as

$$R_p = k_p \left(R_i^{1/2}/k_t \right)[M]$$

where k_p is the propagation rate constant, k_t the termination rate constant, R_i the initiation rate, and [M] the monomer concentration. In the initiation system BP–THF the production of the radicals (ketyl and THF radicals) through the reaction of THF with triplet-excited BP and the rate of reaction of a monomer with the radicals is known to depend on monomer species.[5] The values of $k_p/k_t^{1/2}$ of VTFAc and VAc seem to be different. [M] for VTFAc in the experiment shown in Figure 1 is approximately 8.2 mol/L and that for VAc in Figure 2 10 mol/L. Therefore, $(k_p/k_t^{1/2})R_i^{1/2}$ of VTFAc is larger than that of VAc.

The degree of polymerization (DP) in radical polymerization is represented as

$$\frac{1}{DP} = \frac{k_{trm}}{k_p} + \frac{(k_t R_i)^{1/2}}{k_p[M]} + \frac{k_{trs}}{k_p}\frac{[S]}{[M]}$$

where k_{trm} and k_{trs} are the chain transfer rate constants for a monomer and a solvent. Since the k_{trs} of THF seems to be small and the concentration of low, the third term on the right side of the equation is neglected. In VAc at low temperatures, 1/DP is mainly determined by the second term of the equation,[11] i.e., the first term of the equation is neglected. Therefore, if the first term is neglected for VTFAc too, $(k_t R_i)^{1/2}/k_p[M]$ of VTFAc is concluded to be smaller than that of VAc. The amount of benzophenone does not seem to

influence markedly the rate of polymerization and the degree of polymerization. The syndiotacticity of PVAc prepared at $-78°C$ was 50%, whereas that of PVTFAc was 64%. This suggests that in the bulk polymerization of VAc syndiotacticity-rich PVAc cannot be prepared at $-78°C$.

The polymerization of MMA at $-4°C$ occurred for the liquid mixtures melted after irradiation in a solid state at $-78°C$. The radicals by which MMA polymerizes are produced in the liquid mixtures. The triplet-excited BPs ($^3BP^*$) are produced by irradiation in a solid state though the content is less than that of $^3BP^*$ produced in a liquid mixture. The radicals can be produced by the reaction of THF with $^3BP^*$ in competition with the quenching of $^3BP^*$ by MMA.[5] Thus the production of radicals is considered for the melted mixtures. However, the detailed mechanism is uncertain. Further investigation is necessary.

The rates of polymerization of VTFAc using BA–AZVN and IBA–AZVN were considerably higher than that using AZVN. The enhanced polymerization rate is considered to be due to the aldehydes. Carbonyl compounds, such as benzoin are known to initiate photopolymerization.[12] The similar initiation mechanism is considered in this polymerization, whereas the initiation due to the decomposition by light of the peroxide in BA and IBA is also considered. Peroxide levels of 0.26% and 0.29% were found to be contained in BA and IBA by the iodine method. The initiation of thermal polymerization of acrylonitrile by isobutylaldehyde peroxides has been reported.[13] The degree of polymerization was low due to high chain transfer rate to the aldehydes.

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