Radical Polymerization of Butadiene-1-Carboxylic Acid

YOSHIHUMI BANDO and YUJI MINOURA, *Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan*

Synopsis

The homopolymerization and copolymerization of butadiene-1-carboxylic acid (Bu-1-Acid)(M_1) were studied in tetrahydrofuran at 50°C with azobisisobutyronitrile as an initiator. The initial rate of polymerization was proportional to $[AIBN]^{1/2}$ and $[Bu-1-Acid]^1$. The overall activation energy for the polymerization was 22.87 kcal/mole. For copolymerization with styrene(M_2) and acrylonitrile(M_2), the monomer reactivity ratios r_1, r_2 were determined by the Fineman-Ross method, as follows; $r_1 = 5.55$, $r_2 = 0.08$ (M_2 = styrene); $r_1 = 11.0$, $r_2 = 0.03$ (M_2 = acrylonitrile). Alfrey-Price $Q-e$ values calculated from these values were 6.0 and $+0.11$, respectively. The Bu-1-Acid unit in the copolymer as well as the homopolymer was found from infrared and NMR spectral analyses to be composed of a *trans*-1,4 bond. The hydrogen-transfer polymerization of Bu-1-Acid leading to polyester was attempted with triphenylphosphine as initiator, but did not occur.

INTRODUCTION

The polymerization of alkyl esters of butadiene-1-carboxylic acid, such as methyl, ethyl, 2,3-epoxypropyl β-vinylacrylate have been reported by earlier investigators.[1-4] Recently, the synthesis and polymerization of 1,2,2-trichloroethyl β-vinylacrylate were reported by Bezdek et al.,[5] who performed the radical polymerization and copolymerization with styrene and analyzed its microstructure. However, there were few reports relating to the polymerization of butadiene-1-carboxylic acid in the literature.

Butadiene 1-carboxylic acid (Bu-1-Acid) is one of the simplest butadiene derivatives substituted by carboxylic acid as a polar group and seems to have the combined chemical behavior of butadiene and acrylic acid. In 1926, Kohler et al.[6] synthesized this compound and studied its physical properties and chemical reactivities. Morawetz[7] and Okamura[8] reported the solid-state polymerization of this monomer by γ-irradiation and obtained crosslinked polymer.

In this paper, the authors report the radical homo- and copolymerization of Bu-1-Acid with styrene and acrylonitrile in tetrahydrofuran, as well as an analysis of the microstructure of polymers obtained.

EXPERIMENTAL

Materials

Butadiene-1-carboxylic acid (Bu-1-Acid) was prepared according to the method of Kohler et al.[6] from acrolein and malonic acid in the presence of pyridine. It was purified by repeated recrystalization from petroleum ether, mp 69–72°C (lit. mp[6] 72°C); yields 30%. It was stored in a refrigerator under nitrogen and was further recrystallized from petroleum ether before use. Styrene (St) and acrylonitrile (AN) were purified by the standard method; before use, they were distilled over calcium hydride in a vacuum system under nitrogen. Azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), benzene, and other solvents were purified by the usual methods.

Polymerization Procedure

The required amount of Bu-1-Acid, AIBN, and THF were charged in a Pyrex glass tube, cooled in a Dry Ice–methanol bath and sealed in a vacuum system. The sealed tube was placed in a thermostat maintained at a definite temperature. After polymerization for a given time, the contents of the tube, containing also a small amount of hydroquinone added to prevent gel formation, was poured into a large amount of benzene to precipitate the polymer. The obtained polymer was purified several times by reprecipitation with tetrahydrofuran and benzene. The purification of the copolymers were carried out with THF and petroleum ether.

Measurements

The chemical composition of poly(Bu-1-Acid) and its copolymers with styrene and acrylonitrile was determined from elementary analysis for C, H and N.

The intrinsic viscosity of the polymer was determined in tetrahydrofuran at 30°C by use of an Ubbelohde viscometer.

The infrared spectra of polymers were measured with a Jasco IR-A2 infrared photospectrometer, using films obtained by evaporating THF solution of the polymer on KBr plates.

The H[1]-NMR spectra was measured with a Hitachi Perkin-Elmer R-10 high resolution NMR spectrometer.

The x-ray diffraction pattern of the polymer was taken by using nickel-filtered Cu-Kα radiation.

RESULTS AND DISCUSSION

Polymerizability of Butadiene-1-Carboxylic Acid

Polymerizations of Bu-1-Acid were carried out under various conditions. The reaction conditions and results are summarized in Table I.

When the solid-state polymerization without initiator was carried out, crosslinked polymer was obtained as shown in run 1; therefore, the micro-

TABLE I
Polymerizability of Butadiene-1-Carboxylic Acid (Bu-1-Acid)

Run	Bu-1-Acid, g	Catalyst		PMP, mg[a]	Solvent		Temp, °C	Time, hr	Yield, g	Remark
		Type	Wt, mg		Type	Vol, ml				
1	1	—	—	—	—	—	20	40	0.11	Crosslinked polymer
2	3	AIBN	33	—	Tetrahydrofuran	7	50	6	0.21	1,4-*trans* polymer
3	1.47	TPP	196	52	Nitrobenzene	1.5	100	1/6	0.49	Viscous liquid
4	1.47	TPP	196	52	Acetonitrile	1.5	100	1/6	0.47	Viscous liquid
5	1.47	TPP	196	52	Bulk	—	100	1/15	0.66	Viscous liquid

[a] PMP = *p*-methoxy phenol.

structural analysis could not be performed. The results of radical polymerization of Bu-1-Acid with AIBN in THF are shown in run 2. The poly(Bu-1-Acid) obtained with the radical initiator was soluble in polar solvents such as DMF, THF, DMSO, MeOH, and dioxane and insoluble in nonpolar solvents like benzene, petroleum ether, hexane, and ether. The polymer obtained in run 2 was a white solid and had an apparent melting temperature of around 110°C and an intrinsic viscosity in tetrahydrofuran (20%, 30°C) of 0.3.

Recently, the hydrogen-transfer polymerization of acrylic acid leading to polyester was performed with the use of triphenyl phosphine (TPP) as initiator by Saegusa et al.[9] We tried to obtain polyester derived from Bu-1-Acid. Runs 3, 4, and 5 were carried out under the same conditions as done with acrylic acid. In each case, a dark-red, viscous oil was obtained. These oils were soluble in chloroform and insoluble in ether, tetrahydrofuran and benzene. Their NMR spectra shows that hydrogen-transfer polymerization of Bu-1-Acid leading to polyester did not occur under these conditions.

Structure of Poly(butadiene-1-Carboxylic Acid)

The NMR spectra of the polymer of run 2 shows that the polymerization was proceeded through 1,4 addition rather than through 1,2 and 3,4 addition since the only peak present around 5.4 ppm corresponds to the unconjugated olefinic proton (–CH=CH–).

The infrared spectra of the polymer and monomer (Bu-1-Acid) are shown in Figure 1. The conjugated diene (–C=C–) absorption band at 1600 cm^{-1}, which is characteristic of the monomer, disappeared in the polymer. The infrared spectrum of the polymer has no absorption at about 910 cm^{-1}, characteristic of out-of-plane vibrations of the CH_2 hydrogen of a vinyl group exhibiting 1,2 monomer addition. The region of 675–730 cm^{-1}, where *cis*-disubstituted ethylene absorbs, is also transparent, while a heavy absorption band at 970 cm^{-1} indicates that the polymerization, under the conditions employed, proceeded through *trans*-1,4 addition.

Moreover, from the results of x-ray spectra of the polymer as recorded by a Geiger counter, the polymer had a peak position around $2\theta = 19$°C, near a *trans*-1,4-polybutadiene derivative substituted by a polar group.[10]

Consequently, it was found from the infrared, NMR, and x-ray spectral analyses that poly(butadiene-1-carboxylic acid) obtained with a radical initiator was composed mainly of *trans*-1,4 units.
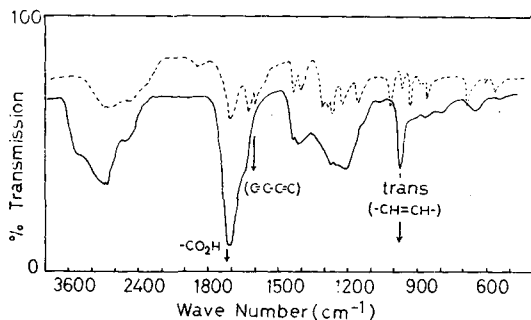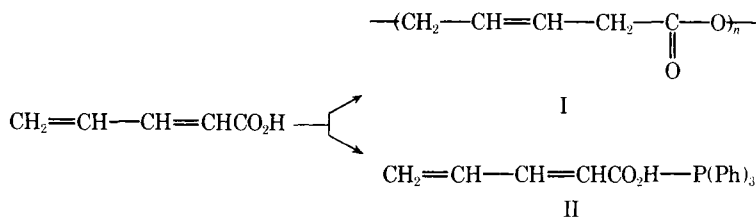
Fig. 1. Infrared spectra of (- - -) Bu-1-Acid and (—) its polymer.

The structures of oils obtained in runs 3, 4, and 5 were assumed from the results of NMR and infrared spectra. The NMR spectra have a large peak at 7.7 ppm due to phenyl group, a singlet peak at 8.9 ppm due to the hydrogen-bonded carboxylic acid proton with triphenyl phosphine, and complex peaks at 5.2–6.7 ppm due to the protons of the diene part. Although their infrared spectra are poor, they had no absorption at 1735 cm^{-1} which is a characteristic absorption band of ester group. Absorption bands at 1600 cm^{-1} and 690 cm^{-1}, characteristic of conjugated diene and phenol groups, respectively, are present. From their infrared and NMR spectrum, the dark red viscous oils seemed to be consistent with the postulated structure (II), as follows.

$$-(CH_2-CH=CH-CH_2-\underset{\underset{O}{\|}}{C}-O)_n-$$

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$$CH_2=CH-CH=CHCO_2H -\!\!\!\Big\langle$$

$$CH_2=CH-CH=CHCO_2H-P(Ph)_3$$

II

Consequently, polyesters such as I are not obtained in the case of Bu-1-Acid.

Kinetics of Radical Polymerization

The polymerization of Bu-1-Acid initiated by AIBN was carried out in THF at temperatures varying over the range 50–80°C, where the concentrations of AIBN and Bu-1-Acid were kept constant at 2.0×10^{-2} and 3.0 mole/l., respectively. The time–conversion curves are shown in Figure 2.

Two series of rate studies of the polymerization of Bu-1-Acid at 50°C were carried out in which the initial concentration of AIBN and then of Bu-1-Acid was varied, while the other was maintained effectively constant. As shown in Figure 3, the rate of polymerization R_p was proportional to $[AIBN]^{1/2}$. Also, it is ordinary in radical polymerization that the intrinsic viscosity of the polymer increases with decreasing the initiator concentration. As shown in Figure 4, the polymerization rate R_p was proportional to the power of [Bu-1-Acid]. Again, the usual phenomena relating to the intrinsic viscosity of the polymer was noted, in that with increasing Bu-1-Acid concentration, the intrinsic viscosity of the polymer also increased.
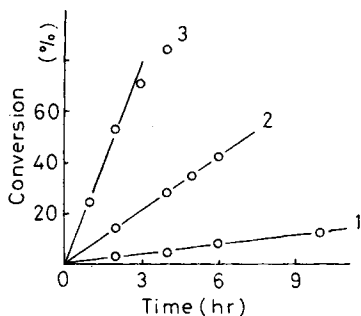
Fig. 2. Polymerization of Bu-1-Acid initiated by AIBN in THF at different temperatures: (1) 50°C; (2) 65°C; (3) 80°C.
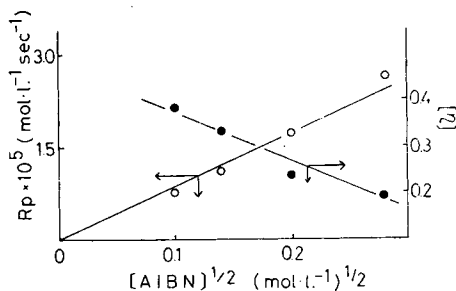

Fig. 3. Variation of the polymerization rate R_p and the intrinsic viscosity $[\eta]$ with the square root of AIBN concentration.   [Bu-1-Acid] = 3.0 mole/l.; temperature, 50°C.

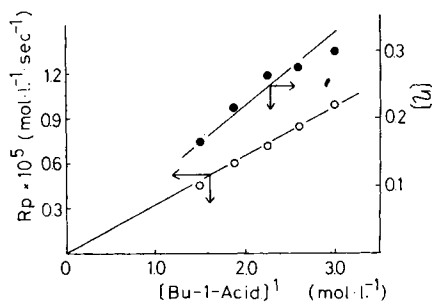Fig. 4. Influence of monomer concentration on rate of polymerization (R_p) and intrinsic viscosity $[\eta]$.   [AIBN] = 2.0 × 10^{-2} mole/l.; temperature, 50°C.

Accordingly, the rate equation for the radical polymerization of Bu-1-Acid in THF at 50°C, using AIBN as an initiator was obtained as follows:

$$R_p = k[\text{AIBN}]^{1/2}[\text{Bu-1-Acid}]^1$$

A plot of log R_p, as inherent viscosity of the polymer versus $1/T$, is shown in Figure 5. From this plot, an Arrhenius activation energy was estimated as 22.87 kcal/mole. Intrinsic viscosity of the polymer increased with increasing $1/T$.
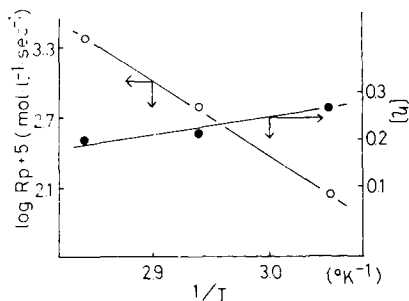
Fig. 5. Influence of temperature on rate of polymerization and intrinsic viscosity $[\eta]$. [Bu-1-Acid] = 3.0 mole/l.; [AIBN] = 2.0 × 10^{-2} mole/l.

No change in microstructure of the poly-(Bu-1-Acid) was noticed on varying the polymerization temperature over the range of 50–80°C. The polymerization of Bu-1-Acid proceeded by 1,4-*trans* addition mechanism at all temperatures studied.

Radical Copolymerization

The radical copolymerizations of Bu-1-Acid (M_1) with styrene (M_2) and acrylonitile (M_2) in THF were carried out by conventional methods. The conversion was controlled within 10% in all cases and the copolymer composition was determined by the C, H, N analysis.

The infrared spectra of the copolymers of Bu-1-Acid with St and AN are shown in Figure 6. From the presence of the strong absorption at 970 cm^{-1} in the spectra, it was found that the Bu-1-Acid units of the copolymer with St are also composed of the *trans*-1,4 bonds. The same result was obtained in the case of the copolymer with acrylonitrile.

Foster et al.[11] reported the effect of comonomer on the microstructure of butadiene copolymer. They mentioned that the percentage of *trans*-1,4 addition increases, the 1,2 addition decreases, and the *cis*-1,4 addition decreases as the styrene content is increased. However, in the case of butadiene-1-carboxylic acid copolymer, the microstructure does not vary. Polymerization proceeded through *trans*-1,4 addition alone at all contents of the copolymer. The same results were obtained in the polymerization of butadiene derivatives[4–7] substituted by polar groups.
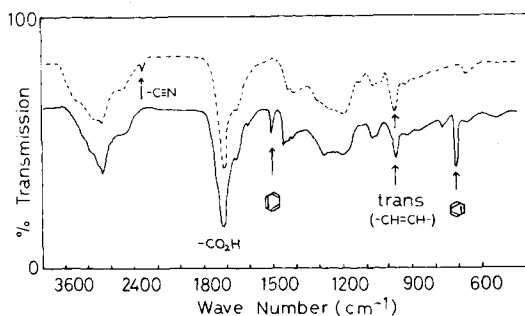

Fig. 6. Infrared spectra of copolymers of Bu-1-Acid: (——) with St and (- -) with AN.
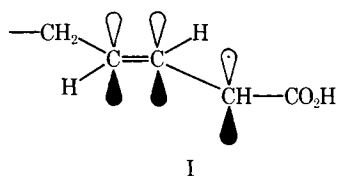
TABLE II
Monomer Reactivity Ratio and Alfrey-Price $Q-e$ values

M_1	M_2	r_1	r_2	Q_1	e_1
Butadiene-1-carboxylic acid	Styrene	5.55	0.08	6.0	+0.11
Butadiene-1-carboxylic acid	Acrylonitrile	11.0	0.03	5.9	+0.10
Glycidyl β-vinyl-acrylate	Styrene	4.79	0.13	4.79	−0.05
Butadiene[b]				2.39	−1.05
Acrylic acid[b]				1.15	+0.77

[a] Data of Iwakura et al.[4]

[b] Data of Brandrup and Immergut.[14]

The *trans*-positioned electron crowds of the propagating radical, conjugated with the allyl groups and carboxyl groups on the same plane, seems to be most stable (Structure I).

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The composition curves are shown in Figure 7. The monomer reactivity ratios r_1, r_2 were determined by the Fineman-Ross method[12] and the Alfrey-Price Q and e values[13] were calculated from them. The values are summarized in Table II, together with those of the monomers reported in the literature.

From Table II, it is evident that the value of Q_1 of Bu-1-Acid is larger than that of butadiene. The high value of Q_1 confirms the resonance stability of the Bu-1-Acid. Moreover, it was observed that the copolymer yields decreased with an increase of St and AN content in the molar feed ratio. Bu-1-Acid acted as if it were a retarding agent for the polymerization of styrene.
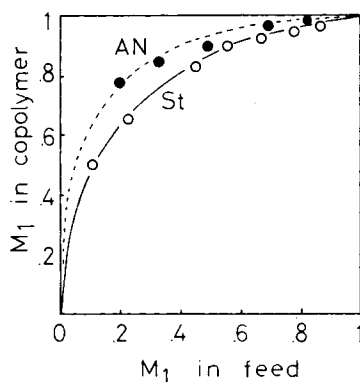

Fig. 7. Copolymer composition curve for Bu-1-Acid (M_1) with styrene (M_2) and acrylonitrile (M_2) in THF: (O) styrene (M_2); (●) acrylonitrile (M_2).

That suggests that the high value of Q_1 of butadiene 1-carboxylic acid ($Q_1 = 6.0$) is due to the stability of the allyl radical involving the participation of carboxyl group.

On the other hand, the strongly negative inductive effect of the carboxylic acid group may account for the positive e value. The e value is a measure of the electron density on the unsaturated part against a standard of styrene -0.8; That of butadiene is negative, while that of acrylic acid is positive. In the case of Bu-1-Acid it seems to be understood easily that the e value is a value intermediate between those of butadiene and acrylic acid. Accordingly, the electron density of the unsaturated diene group conjugated with the carboxylic acid of butadiene-1-carboxylic acid is lower than that of butadiene and greater than that of acrylic acid.

CONCLUSION

Butadiene-1-carboxylic acid was a monomer which was readily polymerized with the use of the radical initiator. The rate equation for the polymerization of Bu-1-Acid followed to the usual one for radical polymerization. The microstructural analysis of the resultant polymers indicated that this monomer always reacted through a *trans*-1,4 addition mechanism at all temperatures and with the use of any comonomer. From the result of the copolymerization, it was found that the Q value of Bu-1-Acid was larger than that of butadiene and that the electron density of the unsaturated part of Bu-1-Acid was much richer than that of acrylic acid.

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