$N_3P_3Cl_2Ph_4$, and $N_3P_3ClPh_5$. These tubes were then exposed at 30° to γ radiation from a cobalt-60 source for 72 hr at a dose rate of 8.7×10^5 rads/hr for a total dose of 6.26×10^7 rads. After irradiation, the tubes were opened and GPC chromatograms of the products were taken. No polymer was present in any of the samples except in the tube containing $(NPCl_2)_3$.

Analytical Techniques. Gel permeation chromatography measurements were made with the use of a Waters Associates ALC/GPC 501 instrument. The columns used were two ⅜ in. by 2 ft stainless steel columns which contained Styragel 10^4 packing. Tetrahydrofuran was employed as a solvent at a flow rate of 2.0 ml min, with samples injected at a concentration of 0.5 wt vol %. A refractive index detector was used. Approximate calibration of the columns was accomplished by means of medium molecular weight polystyrene standards obtained from Waters Associates together with the use of $\bar{M}_n$ and viscosity data for other phosphazenes.[12,13,18,33] Infrared spectra were obained with the use of a Perkin-Elmer 621 Grating Infrared Spectrometer. Solution viscosity data were obtained with the use of a Cannon-Ubbelohde dilution viscometer (size 75) at 30°. Solutions were prepared at concentrations of 1.0, 0.5, 0.33, and 0.25 g/100 ml. The DTA and DSC curves were obtained with the use of Perkin-Elmer instruments.[34]

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A Kinetic Study of Anionic Polymerization of *tert*-Butyl Crotonate

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ABSTRACT: A kinetic study of anionic polymerization of *tert*-butyl crotonate in tetrahydrofuran is presented to confirm that the propagation in that polymerization proceeds via a living mechanism without any side reaction if the temperature is lower than −30°. The propagation rate constant is not affected by initiator species if the same counterion (Li^+) is used. However, the initiation efficiency is found to be low and different with initiator species because of the side reactions occurring in the initiation stage. Moreover, it is found that the ion pairs contribute to the propagation more prominently than the free ions, as in the anionic polymerization of methyl methacrylate. The propagation rate constant of the ion pair is markedly smaller than that for methyl methacrylate, because of the steric hindrance between α and β substituents.

The mechanism of anionic polymerization of α,β-unsaturated carbonyl monomers, especially that of methyl methacrylate (MMA) in polar solvents, is now well clarified.[1–7] Despite the fact that anionic polymerizations, under proper experimental conditions, can give monodisperse samples of poly(methyl methacrylate) (PMMA), it was observed that the deactivation of a part of initiators used always occurs because of various kinds of side reactions such as proton abstraction or addition to the carbonyl group.[1,2] The problems arising from the deactivation may be interesting for the study of the mechanism of polymerization but may be more important if we want to study the physical properties of those samples. Even if a slight amount of side reaction would occur during propagation, the samples obtained could not be suitable for precise measurements. In the anionic polymerization of MMA, it was confirmed by Mita et al.[5] and Löhr et al.[6,7] from their kinetic studies that the side reactions such as carbonyl attack occur only at the initiation stage, and then that the propagation proceeds practically without any side reaction at lower temperatures, producing polymer having a narrow molecular weight distribution.

It was previously reported[8] that another α,β-unsaturated carbonyl compound, *tert*-butyl crotonate (TBC), can be polymerized with 2-methylbutyllithium (2-MeBuLi) in tetrahydrofuran (THF) at −78° on a living mechanism to produce *monodisperse, semiflexible polymers.* In this case, too, the deactivation of the initiator was found to occur. The initiation efficiency, *f*, defined by eq 1 is almost constant (0.50) *if the monomer is very carefully purified,* where [LE] and [I] are the concentrations of the living ends and the initiator added, respectively. Since poly(*tert*-butyl crotonate) (PTBC) is considered to be an important model sample for studying the effect of flexibility of polymer backbone on the physical properties of polymer because of its monodispersity, it is important to confirm that the deactivation of the initiator should occur only at the initiation stage, as it was previously speculated from the constant value of *f* during propagation.[8]

$$f = [\mathrm{LE}]/[\mathrm{I}] \qquad (1)$$

The kinetic study on the anionic polymerization of α,β-unsaturated carbonyl monomers is so far limited to that on MMA.[3–7] Alfrey et al.[9] pointed out that the β substituent decreases the propagation rate in the radical polymerization due to steric hindrance. However, there have been few reports about the effect of β substituent on the propagation rate in the anionic polymerization. Thus, it seems meaningful to study the anionic polymerization kinetics of TBC in comparison with that of MMA. It will be shown that the β substituent decreases the propagation rate remarkably due to the steric hindrance.

Experimental Section

(1) Monomer, Solvents, and Initiators. The monomer TBC was prepared and highly purified in the previous way.[8] The solvent THF was purified also in the way reported previously.[8]

Initiators used here were 2-MeBuLi, *n*-butyllithium (*n*-BuLi), fluorenyllithium (FlLi), and diethylaminolithium (DEALi). The 2-MeBuLi and *n*-BuLi in *n*-hexane solutions were prepared in the previous way.[8] FlLi was prepared by the reaction of fluorene with lithium in THF. DEALi was prepared by the reaction of the above *n*-BuLi solution with dimethylamine. The chemical composition of DEALi was confirmed by acid titration.[10] The concentrations of those initiators [I] were determined by acid titration, as reported previously.[8] A required amount of each initiator solution was sealed in a fragile glass capsule containing a glass stirrer tip in vacuo.

(2) Dilatometry. There are various methods for measuring the rate of polymerization, for example, flow method, spectroscopic method, and dilatometry. We chose the dilatometry since the polymerization rate in vacuo can be easily observed with stirring of the sample solution.

The dilatometer used here is shown in Figure 1. A fragile capsule A, containing a certain amount of the initiator solution together with a glass magnetic stirrer tip B, was introduced from C into the dilatometer vessel D (about 25 ml volume) and the entrance C is sealed off. After this apparatus was evacuated to 10^{-6} mm and sealed off, the whole apparatus was washed with a THF solution of dipotassium salt of α-methylstyrene tetramer in E, which was afterwards recovered into the vessel F and sealed off. Then, TBC solution in G was transferred through the capillary H (about 2 mm diameter) into the vessel D. The dilatometer part was sealed off at the position I and cooled to a required temperature. The meniscus height of solution was adjusted by transferring an excess solution into the pocket J. The polymerization was initiated instantly by crushing the initiator capsule A with a magnetic stirrer tip B.

The polymerization was carried out in a double thermostat, the temperature of which was manually kept constant within ±0.2°. The temperature was determined by observing the meniscus in a monitoring dilatometer containing THF, which had almost the same volume as the dilatometer for measurements but had a finer capillary (about 1 mm diameter). The sensitivity of the THF thermometer is 0.01°. The correction for the temperature fluctuation was given to the observed meniscus height of the dilatometer, but the correction was almost negligible. After the meniscus reached an equilibrium level, the dilatometer was immersed in a liquid nitrogen bath and methanol was added to the viscous solution after opening the dilatometer. The precipitated polymer was collected, washed with fresh methanol, and dried in vacuo.

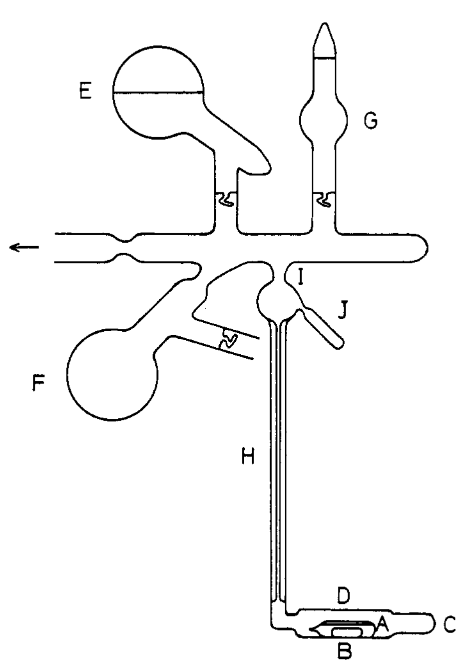

Figure 1. Dilatometer; symbols are shown in text.

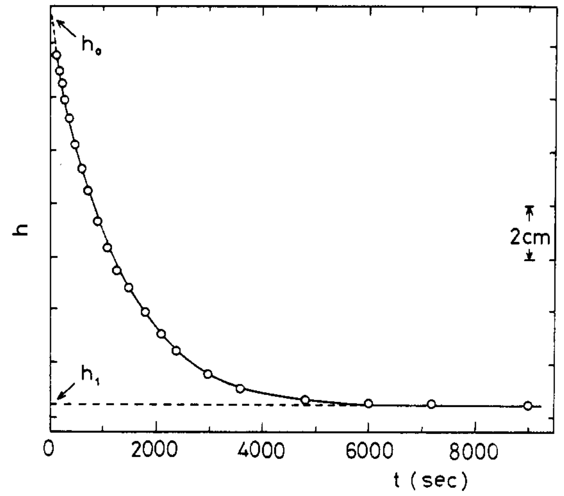

Figure 2. An example of variation of meniscus height *h* with time *t* in the polymerization of experiment no. 5 in Table I.

Figure 2 shows an example of the variation of the meniscus height *h* with time *t*. The difference between *h* and the height at $t = 0$, h_0, is proportional to the conversion x. If the meniscus height at the complete conversion is expressed by h_1, the conversion x at time *t* is given by

$$x = (h_0 - h)/(h_0 - h_1) \qquad (2)$$

or

$$1 - x = (h - h_1)/(h_0 - h_1) \qquad (3)$$

The value of h_0 cannot directly be determined, since there is a change in the meniscus height when the initiator capsule is broken, due to, for example, the heat of mixing. However, in the polymerization of TBC in THF, the final equilibrium conversions reached almost 100% within the error of 2% after a sufficient time. Therefore, the value of $(h - h_1)$, which is proportional to $(1 - x)$, can be determined experimentally.

To the living polymerization, where the rate of initiation is much faster than that of propagation, the first-order relation is applicable

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{LE}][\mathrm{M}] \qquad (4)$$

where [M] is the monomer concentration at time *t* and k_p is the propagation rate constant. If [LE] is constant during the polymerization, eq 4 can be transformed into eq 5 by integration, such as

Table I
Anionic Polymerization of TBC with 2-MeBuLi in THF

Expt no.	Temp, °C	$[M]_0$[a], mol $l.^{-1}$	[I], mol $l.^{-1}$	[LE], mol $l.^{-1}$	f	k_p, l. mol^{-1} sec^{-1}
1	−78				0.50[b]	
2	−75	6.1×10^{-1}	2.9×10^{-3}	1.2×10^{-3}	0.42	0.14
3	−75	6.2×10^{-1}	5.3×10^{-3}	2.4×10^{-3}	0.45	0.13
4	−75	6.1×10^{-1}	6.6×10^{-3}	2.5×10^{-3}[c]	0.38	0.13
5	−66	6.2×10^{-1}	3.7×10^{-3}	1.3×10^{-3}	0.35	0.45
6	−60	6.0×10^{-1}	3.0×10^{-3}	1.2×10^{-3}[c]	0.41	0.67
7	−40	6.2×10^{-1}	2.9×10^{-3}	0.99×10^{-3}[c]	0.34	3.5
8	−30	6.4×10^{-1}	3.7×10^{-3}	1.2×10^{-3}	0.32	6.0
9	0	6.1×10^{-1}	3.3×10^{-3}	1.1×10^{-3}	0.33	7.0[d]
10	13	6.4×10^{-1}	3.7×10^{-3}	1.1×10^{-3}	0.30	15[d]

[a] Initial monomer concentration. [b] Average value in the previous paper.[8] [c] Calculated value from [η]. Others were determined by osmometry. [d] Calculated value from initial slope.

Table II
Anionic Polymerization of TBC in THF at −40°

Expt no.	Initiator	$[M]_0$, mol $l.^{-1}$	[I], mol $l.^{-1}$	[LE], mol $l.^{-1}$	f	k_p, l. mol^{-1} sec^{-1}
7	2-MeBuLi	6.2×10^{-1}	2.9×10^{-3}	0.99×10^{-3}[a]	0.34	3.5
11	*n*-BuLi	4.4×10^{-1}	4.4×10^{-3}	1.2×10^{-3}[a]	0.27	3.4
12	FlLi	4.6×10^{-1}	3.2×10^{-3}	1.2×10^{-3}	0.38	2.7
13	DEALi	4.7×10^{-1}	2.5×10^{-3}	1.8×10^{-3}	0.72	3.8

[a] Calculated value from [η]. Others were determined by osmometry.

$$\log(1 - x) = -(k_p/2.303)[\mathrm{LE}]t \tag{5}$$

Insertion of eq 3 into eq 5 gives

$$\log(h - h_1) = -(k_p/2.303)[\mathrm{LE}]t + \log(h_0 - h_1) \tag{6}$$

Thus, from the plot of log $(h - h_1)$ vs. t, both k_p and h_0 can be determined if [LE] is known.

The concentration of the living end, [LE], was calculated from the yield and the molecular weight of the polymer obtained as reported previously.[8] The molecular weight was mainly determined by the osmotic pressure method or partly calculated from the limiting viscosity number using the following equation[8]

$$[\eta] = 1.74 \times 10^{-5} M_n^{0.96} \qquad (10^4 < M_n < 10^5) \tag{7}$$

where [η] is the limiting viscosity number in toluene at 25° and M_n is the number-average molecular weight of the polymer. The error arising from the use of [η] to calculate [LE] may be negligible since eq 7 was determined by using a series of the samples polymerized under the same experimental conditions as in this work. The initiation efficiency f was also calculated from the ratio of [LE] to the concentration of the initiator used, [I], according to eq 1.

Results

The polymerization of TBC in THF with 2-MeBuLi was carried out at various temperatures. Figure 3 gives examples of the first-order plots according to eq 6. Good linear relationships between log $(h - h_1)$ and t were obtained up to 90% conversions or more if the temperature was below −30°. In the experiments at the temperatures higher than −30° (experiment no. 9 and 10 in Table I), the linear relationship appears to hold only at low conversions, as is also shown in Figure 3. The values of k_p in these cases were estimated from the initial slopes. However, it is to be noted that the conversions reached 100% in all experiments. In Table I, the k_p values obtained with various concentrations of 2-MeBuLi at −75° are shown (experiment no. 2–4). From this table, k_p appears to be only slightly dependent on [LE] under the present experimental conditions.

Various kinds of lithium alkyls were used to investigate the effect of the initiator species on the rates of polymerization. The linearity between log $(h - h_1)$ vs. t holds well in these experiments, too. The values of k_p and f obtained were shown in Table II. The rate constants k_p determined with various initiators are almost identical.

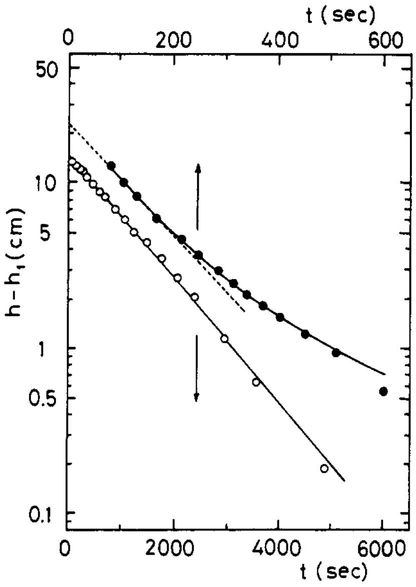

Figure 3. Examples of the first-order plots for the polymerization of experiment no. 5 (open circles) shown in Figure 2 and experiment no. 9 (filled circles) in Table I.

All experimental results, explained above, show that no side reaction does occur during the propagation if the temperature is below −30°. Therefore, the anionic polymerization of TBC in THF at lower temperatures proceeds on a living mechanism, in agreement with our previous conclusion.[8] Since the plot of log $(h - h_1)$ vs. t is not linear at temperatures higher than −30°, it is likely that there are some side reactions in the propagation at higher temperatures. This fact is similar to that observed in the polymerization of MMA, but the conversion of MMA does not reach 100%,[5] whereas that of TBC reaches 100%.

The initiation efficiency f is always lower than unity and different with different initiator species, as can be seen in

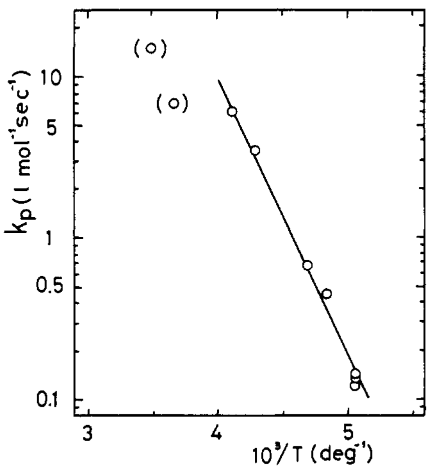

Figure 4. The Arrhenius plot of k_p for polymerization of TBC with 2-MeBuLi in THF.

Table II. That is, f with DEALi is very high, though its k_p is almost the same as those with other lithium alkyls. Moreover, Table I shows that f decreases with increasing temperature. Therefore, it may be concluded that some side reactions surely occur at the initiation stage.

Discussion

There exist, in general, two species of living ends in anionic living polymerization, that is, free ions and ion pairs. According to Szwarc[11] and Schulz,[12] the overall propagation rate constant k_p may be divided into two parts by eq 8, if there are much less free ions than ion pairs

$$k_p = k_{(\pm)} + k_{(-)}K_D^{1/2}/[\mathrm{LE}]^{1/2} \qquad (8)$$

where $k_{(\pm)}$ and $k_{(-)}$ are the rate constants of ion pair and free ion, respectively, and K_D is the dissociation constant of the ion pair. In the polymerization of TBC with 2-MeBuLi in THF at −75°, a plot of k_p vs. $[\mathrm{LE}]^{-1/2}$ gives the values of $k_{(\pm)}$ and $k_{(-)}K_D^{1/2}$ to be 0.1 (l. mol^{-1} sec^{-1}) and 1×10^{-3} (l.$^{1/2}$ mol$^{-1/2}$ sec^{-1}), respectively. It may be concluded that the contribution of ion pair is more important than that of free ion in the anionic polymerization of TBC, as well as in the polymerization of MMA.[3-7] This $k_{(\pm)}$ value for PTBC$^-$Li$^+$ at −75° is markedly smaller than that for PMMA$^-$Na$^+$ (60 at −75° [5] and 100 at −78° [6,7]) and that for PMMA$^-$Cs$^+$ (80 at −78° [6,7]). Furthermore, Figure 4 shows the Arrhenius plot of k_p, which gives the apparent activation enthalpy to be about 7 kcal mol^{-1}. The value is comparable to those for PMMA$^-$Na$^+$ and PMMA$^-$Cs$^+$.[6,7] Therefore, the low value of k_p for TBC is due to the low activation entropy in the propagation of TBC which has a more hindered structure. Thus, it may be concluded that the difference between the anionic polymerization rates of MMA and TBC is mainly due to the steric hindrance between the *tert*-butyl ester group and the β-methyl group, as was pointed out by Alfrey et al.[9] for radical polymerization. It is striking that the β substituent decreases the propagation rate so markedly.

Finally, it seemed somewhat unreasonable[8] that the side reaction occurs only in the initiation stage but does not occur during propagation if the temperature is below −30°, but it may be understandable from the molecular structures of those active centers, as was pointed out by Tsuruta[13] and Mita.[14] The active center during propagation is the enolate anion which has a delocalized charge, whereas the initiator is the carbanion having a localized charge. In our previous study,[8] we also found isopentane but did not find *tert*-butyl alcohol, as was reported by Tsuruta et al. in their study on the reaction between methyl acrylate and *n*-butyllithium.[1,2] Therefore, the side reaction *may* be mainly the hydrogen abstraction.

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