Preparation and properties of poly(*sec*-butyl crotonate)

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Poly(*sec*-butyl crotonate) (poly(SBC)) was prepared by anionic polymerization. 1,1-Diphenylhexyllithium was found to be an effective initiator. Poly(SBC) showed the same optical properties as poly(methyl methacrylate) (poly(MMA)) but different features: poly(SBC) had a high glass transition temperature (T_g) and very high extensibility below T_g, in comparison to poly(MMA). Poly(SBC) can be expected to find applications as an optical material having high flexibility and high service temperature.

(Keywords: poly(*sec*-butyl crotonate); anionic polymerization; optical properties)

Introduction

Acryl polymers, such as poly(methyl methacrylate), have been widely used as optical materials. However, acryl polymers have a low service temperature. Alkyl crotonate and alkyl methacrylate are both α,β-unsaturated esters. A difference exists only in the position of the methyl group: α-methyl in alkyl methacrylate and β-methyl in alkyl crotonate. Hence, poly(alkyl crotonate) is expected to show an equally high refractive index and a higher service temperature than poly(alkyl methacrylate).

Alkyl crotonates have been polymerized by anionic polymerization by several investigators[1–6]. However, detailed data on characterization and properties have not been reported. The rigorous anionic polymerization of tert-butyl crotonate (TBC) was performed by Kitano *et al.*[7,8]. They proved that TBC can be polymerized quantitatively in yield with 2-methylbutyllithium in tetrahydrofuran (THF); the resultant polymer had a very narrow molecular weight distribution. However, poly(TBC) showed semiflexibility, which may be due to high steric hindrance between the methyl group at the β-position and the tert-butyl ester group at the α-position, and semicrystallinity. These features are a great disadvantage in processing. The semiflexibility and semicrystallinity are expected to decrease in poly(*sec*-butyl crotonate) (poly(SBC)).

This paper briefly shows the results of anionic polymerization of *sec*-butyl crotonate (SBC) and the interesting properties of the resultant polymer.

Experimental

Materials. *sec*-Butyl crotonate was purchased from Tokyo Kasei Kogyo Co., Ltd as EP grade. The monomer was treated with aqueous sodium hydroxide and then distilled under reduced pressure. Further purification of the monomer was carried out in an all-glass apparatus equipped with breakseals under a reduced pressure of 1×10^{-3} Pa or lower. After being dried with calcium hydride, the monomer was transferred into a vacuum apparatus and purified by distillation with sodium mirror, and then with triethylaluminium in several stages[9]. Finally, the monomer was redistilled in the presence of triethylaluminium prior to polymerization.

Initiators used were n-butyllithium (n-BuLi), *sec*-butyllithium (*sec*-BuLi), and 1,1-diphenylhexyllithium (DPHL). They were prepared and purified as described previously[9,10]. n-BuLi and *sec*-BuLi were diluted with purified n-heptane. DPHL was diluted with purified benzene. The concentrations of the initiators were determined by titration with a standard HCl solution.

Polymerization. Anionic polymerizations of SBC were carried out in a sealed glass apparatus under a pressure of 1×10^{-3} Pa or lower, using essentially the same procedure as has been reported previously[9–12]. The polymerization solvent was THF and the temperature varied from 195 to 243 K. After being quenched with methanol, the polymers were precipitated into an excess of methanol. The purified polymers were freeze-dried from the benzene solutions for 24 h.

Characterization. Number-average molecular weight (M_n) and molecular weight heterogeneity index (M_w/M_n) were measured by g.p.c. at 298 K using an HLC type 803 instrument (Tosoh Ltd) with a refractive index detector and a set of two high-resolution GMH6 columns (600 mm length and 7.8 mm inner diameter). THF was used as an eluent. The column set was calibrated with poly(SBC)s having fairly narrow molecular weight distributions, which were obtained by fractionation of the polymers prepared in this study. Fractionation was carried out by g.p.c. at 298 K using an HLC type 837 fully automatic instrument (Tosoh Ltd)[9]. Number-average molecular weights of the fractionated polymers were determined by osmometry in toluene at 303 K with a Hewlett-Packard type 502 high-speed membrane osmometer or with a Corona type M114 vapour pressure osmometer. During vapour pressure osmometry, an apparatus constant was determined with a standard polystyrene ($M_n = 9.1 \times 10^3$, $M_w/M_n = 1.0_2$). The glass transition temperature (T_g) was determined by d.s.c. with a Seiko DSC-20 instrument at the temperature scanning

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rate of 10 K min^{-1}. Intrinsic viscosities of the fractionated polymers, $[\eta]$, were measured in toluene at 303 K with a capillary viscometer of a modified Ubbelohde type. Gas permeability coefficients were measured by the vacuum method.

Results and discussion

Anionic polymerization of SBC. *Table 1* shows the results of polymerization of SBC in THF with various anionic initiators. When n-BuLi was used as an initiator (run no. 1), a polymerized product was obtained, but both the yield and the initiation efficiency were very low. A side reaction, mainly due to the attack of carboanion on the ester group of SBC, seems to be dominant, and the polymerization of SBC may proceed with a very low rate of propagation in this system. When *sec*-BuLi was used, the values of yield and initiation efficiency increased (runs 2–4). The use of DPHL as an initiator in run no. 5 leads to a quantitative yield and an increase in initiation efficiency but no particular change in molecular weight distribution. The initiation efficiency of DPHL is practically unchanged, even at higher ratio of monomer to initiator (run no. 6). A bulky initiator, DPHL, effectively suppresses the side reaction in the initiation step. In the *sec*-BuLi/THF and DPHL/THF systems, however, the solution in the reactor becomes increasingly viscous with time, and finally gel appears in the solution, particularly at lower temperature (195 K),

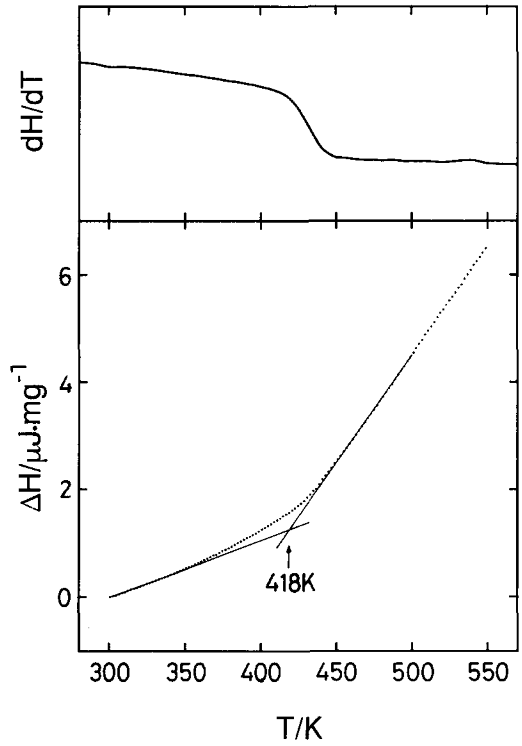

Figure 1 D.s.c. pattern and the corresponding integration curve of poly(SBC). $M_n = 7.0 \times 10^4$, $M_w/M_n = 1.1_6$

Table 1 Anionic polymerization of *sec*-butyl crotonate in THF

Run no.	Monomer (mmol)	Initiator		Conc.[a] (%)	Time (h)	Temp. (K)	Yield (%)	$10^{-3}M_k$[b]	$10^{-3}M_n$[c]	M_w/M_n[c]	f[d]
		Name	(mmol)								
1	$84._3$	n-ByLi	2.8_4	$11._0$	40	233	10	0.5	11	1.4_7	0.05
2	$66._5$	*sec*-BuLi	2.1_5	$30._3$	24	243	61	2.7	23	1.8_3	0.12
3	$63._4$	*sec*-BuLi	1.2_5	$12._1$	50	195	79	5.8	23	1.7_8	0.25
4	$69._0$	*sec*-BuLi	0.7_3	$12._9$	50	195	64	8.7	26	1.8_4	0.33
5	$47._6$	DPHL	0.5_1	$10._5$	44	195	95	13	25	1.9_3	0.52
6	$37._3$	DPHL	0.1_6	$8._3$	44	195	42	14	32	1.9_9	0.44

[a] Monomer concentration (w/v)
[b] Kinetic molecular weight, M_k was calculated from the polymer yield and the ratio of amounts of monomer to initiator
[c] M_n and M_w/M_n were calculated by g.p.c. on the basis of calibration with fractionated poly(*sec*-butyl crotonate)s
[d] Initiation efficiency f was estimated from the ratio of M_k to M_n

Table 2 Comparison of properties between poly(*sec*-butyl crotonate) (poly(SBC)) and poly(methyl methacrylate) (poly(MMA))

Property	Poly(SBC)	Poly(MMA)	Remarks[a]
Transmissivity (%)	92	92[b]	1 mm thickness, 830 nm
Refractive index, n_D	1.48	1.49[c]	ASTM D542
Density (g cm^{-3})	1.04	1.18[c]	303 K
Glass transition temperature (K)	418	378[c]	d.s.c., 10 K min^{-1}
Tensile strength (kgf cm^{-2})	220	730[b]	ASTM D638
Tensile elongation at break (%)	45	5[b]	ASTM D638
Oxygen permeability coefficient (cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1})	1.1×10^{-9}	3.5×10^{-11}[b]	298 K
Nitrogen permeability coefficient (cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1})	2.9×10^{-10}	9.8×10^{-12}[b]	298 K

[a] Measured at 296 K unless otherwise specified
[b] Measured in this work, using a commercially available poly(MMA) (Acrypet V, Mitsubishi Rayon Co., Ltd)
[c] Cited from ref. 14

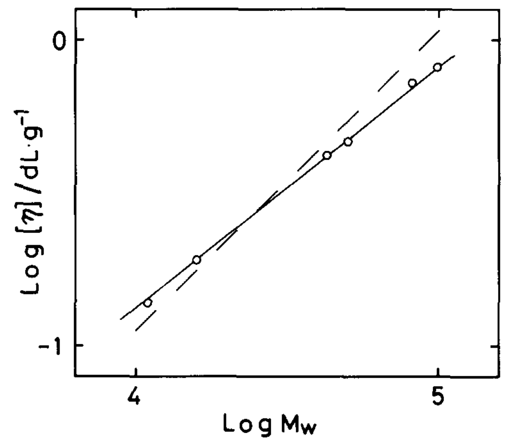

Figure 2 Double logarithmic plot of intrinsic viscosity in toluene at 303 K against weight-average molecular weight for fractionated poly(SBC). $M_n = 9.2 \times 10^3$–8.7×10^4, $M_w/M_m = 1.1_4$–1.2_4. ---, poly(TBC) in toluene at 298 K (ref. 7).

although the gel disappears at room temperature. Such a high viscosity and a heterogeneity in solution may lead to rather low molecular weight and broad molecular weight distribution. It seems to be difficult to obtain a sample of poly(SBC) having high molecular weight.

Properties of poly(SBC). It is interesting to compare the properties of poly(SBC) with those of poly(tert-butyl crotonate) (poly(TBC)) and poly(methyl methacrylate) (poly(MMA)).

Figure 1 shows the d.s.c. pattern of poly(SBC) and the corresponding integration curve. A change due to the glass transition can be found at 418 K. A crystalline melting point was found in poly(TBC)[7] near 525 K, but was not observed in poly(SBC).

Figure 2 shows the relationship between $[\eta]$ and molecular weight. Thus, we have the following Mark–Houwink–Sakurada equation for poly(SBC) in toluene at 303 K:

$$[\eta] = 9.3 \times 10^{-5} M_w^{0.79} \qquad (1)$$

It should be noted that the value of the exponent, $a = 0.79$, is typical for a flexible polymer in a good solvent[13]. This is in contrast to the value of a for poly(TBC) ($a = 0.96$), which shows semiflexibility of the poly(TBC) chain[13], as shown by the broken line in *Figure 2*. It can be concluded that poly(SBC) is an amorphous polymer with a flexible backbone.

Other properties, including T_g, are listed in *Table 2*. For comparison, *Table 2* also shows the corresponding values for poly(MMA), some of which were measured in this work. Optical properties, such as transmissivity and refractive index, are the same for both polymers. However, other physical properties of poly(SBC) are different from those of poly(MMA), for example poly(SBC) showed lower density. Surprisingly, poly(SBC) can be extended up to 1.5 times in length below T_g. Such a high extensibility in the glassy state has not been found in other amorphous polymers. This may arise from a comparatively large free volume due to steric hindrance between β-methyl and *sec*-butyl ester groups. This speculation is supported by the higher gas permeability coefficients for poly(SBC) than for poly(MMA). Poly(SBC) can be expected to find applications as an optical material having high flexibility and high service temperature.

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