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Remarkable Influence of Tacticity on Liquid Crystallinity of Polymethacrylates with Biphenyl Moiety as Mesogenic Group

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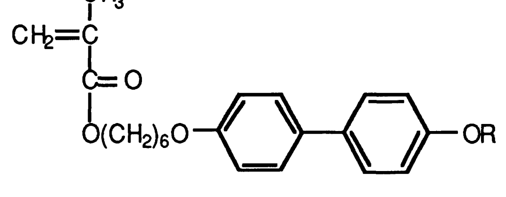
Two methacrylates with a biphenyl moiety as a mesogenic group were anionically polymerized with t-butylmagnesium bromide in toluene, chloroform, and tetrahydrofuran at low temperature. Differential scanning calorimetric analysis of the highly isotactic and syndiotactic polymethacrylates obtained indicated that tacticity of the polymers greatly influences their liquid crystallinity.

Various liquid crystalline polymers with a mesogenic group on a side chain have been prepared.[1)] However, almost no information on the influence of tacticity on liquid crystallinity is available except for the study by Ringsdorf and coworkers[2)] who prepared poly[6-[4-(4-methoxyphenyl)phenoxy]hexyl methacrylate] (poly-**1**) with both about 65% triad isotacticity and syndiotacticity, and found clear dependence of liquid crystallinity of the polymer on tacticity.

In the present study, we prepared poly-**1** and poly[6-[4-[4-[(S)-2-methylbutoxy]phenyl]phenoxy]hexyl methacrylate] (poly-**2**) of higher isotacticity (> 91%) and syndiotacticity (> 84%) by anionic polymerization and investigated their liquid crystallinity mainly by differential scanning calorimetry (DSC). Two polymethacrylates showed almost opposite dependence of liquid crystallinity on tacticity.



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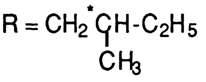
2 : 

$R = CH_2\overset{*}{C}H(CH_3)\text{-}C_2H_5$

6-[4-(4-Methoxyphenyl)phenoxy]hexyl methacrylate (**1**) was synthesized according to the method by Finkelmann.[1] 6-[4-[4-[(S)-2-Methylbutoxy]phenyl]phenoxy]hexyl methacrylate (**2**) was prepared in a similar procedure. The monomers were purified by column chromatography (silica gel, diethyl ether) and recrystallized from diethyl ether and hexane. DSC measurement indicated that **1** had a mesophase from 58.6 °C to 70.3 °C and **2** had only melting point at 54.3 °C.

Table 1 shows the results of anionic and radical polymerizations. Anionic polymerization was carried out under dry nitrogen with t-butylmagnesium bromide (t-BuMgBr) at low temperature for 24 h.[3] In anionic polymerization in toluene, the polymers precipitated during the polymerization. This resulted in low yield and low molecular weight of the polymers. However, the polymerization in chloroform greatly improved these defects giving the highly isotactic polymers with higher molecular weights in better yields. This improvement seems to be ascribed to high solvability of the polymers in chloroform which is a good solvent for most polymethacrylates. Although chloroform has scarcely been used as a solvent for anionic polymerization,[4] this solvent appears interesting and useful for obtaining isotactic polymethacrylates by anionic polymerization. The polymerization in THF afforded highly syndiotactic polymers. It has been shown that the polymerization of methacrylates with Grignard reagents in THF usually gives syndiotactic polymers.[5,6] The tacticity of the polymers was determined by analyzing ^{1}H NMR spectra of poly-**1** and ^{13}C NMR spectra of poly-**2**.

Table 1. Polymerization of **1** and **2** for 24 h[a]

No.	Monomer	Initiator	Solvent	Temp °C	Yield %	Mn[b] x 10^{-3}	Mw[b]/Mn	Tacticity / % mm	mr	rr	Transition temperature / °C[c] T1	T2	T3	T4
1	1	t-BuMgBr	Toluene	0	31.2	1.9	4.25				-	-	-	130.1
2	1	t-BuMgBr	CHCl3	-60	78.6	7.3	2.21				-	-	-	136.4
3	1	t-BuMgBr	CHCl3	-60	27.6	10.1	2.95	91	7	2	-	-	-	135.0
4	1	t-BuMgBr	THF[d]	-78	44.1	10.4	1.41	1	14	85	116.7	-	128.6	130.9
5	1	AIBN[e]	Toluene	60	81.2	12.6	2.26	2	32	66	117.3	119.3	128.6	131.7
6	2	t-BuMgBr	Toluene	-78	21.0	3.6	1.79				92.0	93.9	100.2	105.5
7	2	t-BuMgBr	CHCl3	-60	81.8	7.8	1.81				94.1	97.1	105.2	110.8
8	2	t-BuMgBr	CHCl3	-60	63.1	10.6	2.33	92	8	0	95.5	97.9	106.6	112.6
9	2	t-BuMgBr	THF[d]	-78	96.9	11.7	1.45	4	12	84	-	-	-	123.5
10	2	AIBN[e]	Toluene	60	84.4	14.4	2.46	3	38	59	-	-	-	121.0

a) Monomer 0.5 g, [Monomer] / [Initiator] =20 (#3: 40, #8: 30), solvent 10 ml (#4 & 6 15 ml), #1 polymerized for 4 h.
b) Determined by GPC calibrated with standard polystyrene samples.
c) Determined by DSC measurement at 2nd heating (5 °C / min).
d) Tetrahydrofuran.
e) α,α'-Azobisisobutyronitrile.

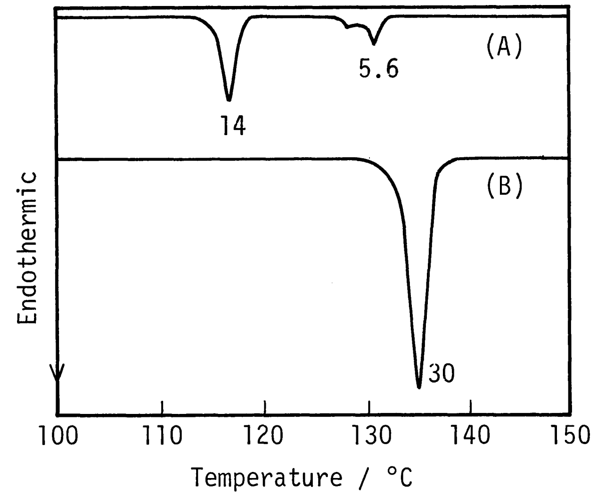


Fig. 1. DSC thermograms of syndiotactic (# 4) (A) and isotactic (# 3) (B) poly-**1** (2nd heating, 5 °C/min. The numbers correspond transition enthalpy (J g^{-1})).

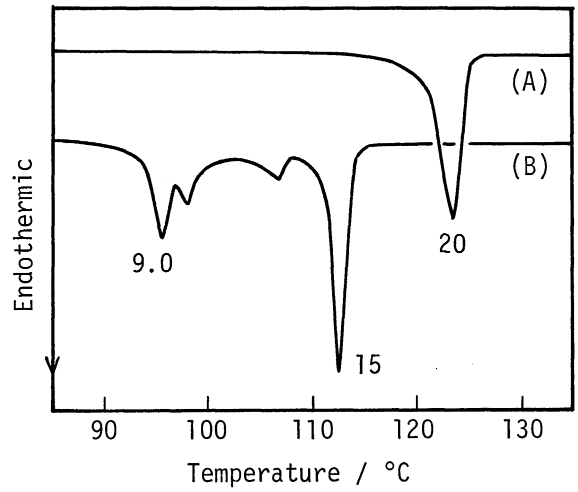


Fig. 2. DSC thermograms of syndiotactic (# 9) (A) and isotactic (# 8) (B) poly-**2** (2nd heating, 5 °C/min. The numbers correspond transition enthalpy (J g^{-1})).

Figure 1 shows the DSC curves of the isotactic and syndiotactic poly-**1** at second heating. Syndiotactic poly-**1** showed three endothermic peaks for phase transition below about 130 °C, whereas isotactic poly-**1** showed only one endothermic peak at about 135 °C. Ringsdorf et al. observed similar DSC peaks for their syndiotactic poly-**1**, but two peaks for the isotactic poly-**1**.[1)] In the investigation by polarizing microscopy, syndiotactic poly-**1** exhibited the two kinds of liquid crystalline phases, which appear to be assigned to nematic phase with Schlieren texture and smectic phase. Isotactic poly-**1** seemed to show only the transition from crystalline phase to isotropic melt. In cooling DSC scan, isotactic poly-**1** also exhibited a single exothermic peak at 126.3 °C. Most isotactic polymethacrylates show higher flexibility of polymer chain than syndiotactic ones.[7)] However, transition temperature of isotactic poly-**1** was higher than those of syndiotactic poly-**1**. The higher transition enthalpy of the isotactic polymer may be associated with its higher transition temperature.

In the DSC analysis of poly-**2** (Fig. 2), isotactic poly-**2** exhibited the four endothermic peaks for phase transition. However, syndiotactic poly-**2** obtained by anionic polymerization in THF and by radical polymerization exhibited only one endothermic peak probably due to the transition from crystalline phase to isotropic melt. Polarizing microscopic investigation revealed that syndiotactic poly-**2** underwent the transition due to only melt, but isotactic poly-**2** displayed the transition due to the existence of liquid crystalline phases which may be S_A phase at 111.1 °C with a fan-shape texture and S_{C}^{*} phase at 106.0 °C with a broken fan-shape texture. The fact that the only isotactic poly-**2** obtained by anionic polymerization exhibited the clear liquid crystalline phase is noticeable because this polymer can not be prepared by radical polymerization which usually affords syndiotactic or atactic polymers.

Although the transition temperature of the polymers shifted depending on the molecular weight, the patterns of DSC thermograms were not varied by the molecular weight. The isotactic poly-**1** (# 2) was fractionated by GPC. The resulting poly-**1** with narrow molecular weight distribution (Mw/Mn = 1.16–1.24, Mn = 48900–5700) showed almost the same patterns of DSC curve as that of the original poly-**1**. The thermal property of the polymers did not depend greatly on the molecular weight and its distribution. Therefore, it is concluded that these two polymethacrylates, poly-**1** and poly-**2**, displayed almost opposite dependence of liquid crystallinity on tacticity.

References

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6) The polymerization of **1** has already been carried out with t-BuMgBr in THF, but the tacticity of the polymer has not been determined. (N. Koide, T. Kumada, and K. Iimura, The 14th Japanese Symposium on Liquid Crystals, Sendai, 1988, Abstr., 3D310 (p. 264)).
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