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Registry No. 1 (homopolymer), 90385-55-0; 1 (SRU), 85609-98-9; 2 (homopolymer), 30729-36-3; 2 (SRU), 26099-71-8; (1)(2) (copolymer), 124921-53-5; (4-acetoxybenzoic acid)(3-chloro-4-acetoxybenzoic acid) (copolymer), 124921-51-3; (3-chloro-4-(trimethylsiloxy)benzoyl chloride)(4-(trimethylsiloxy)benzoyl chloride) (copolymer), 124921-52-4.

Polycondensation Catalyzed by a Palladium Complex. 2. Synthesis and Characterization of Main-Chain Type Liquid Crystalline Polymers Having Distyrylbenzene Mesogenic Groups

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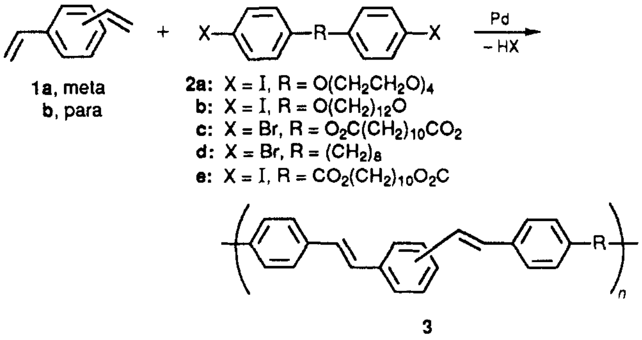
ABSTRACT: Polymers having *trans,trans*-distyrylbenzene units in the main chain were synthesized by the Heck reaction of *p*-(or *m*-)divinylbenzene with bis(halobenzene) derivatives that have a flexible chain such as a longer alkyl or poly(oxyethylene) group. The product polymers exhibited thermotropic liquid crystallinity, which was characterized by using DSC and an optical microscope with cross-polarizers. Smectic textures were observed in the mesophases of polyesters and polyethers derived from *m*-divinylbenzene.

Introduction

Very recently, we have reported a novel polycondensation catalyzed by a palladium complex.[1] Polyester and polyamide having cinnamoyl units were synthesized by the Heck reaction,[2] i.e., a coupling reaction between aryl halide moieties and C=C double bonds of acrylic derivatives. Some of the product polymers showed mesophases. This article deals with the further investigation of this novel polycondensation,[3] preparing liquid crystalline (LC) polymers that consist of distyrylbenzene groups in the main chains.[4,5]

It is well-known that a main-chain type thermotropic LC polymer consists of two constituents, i.e., a rigid segment such as biphenyl group or stilbene group and a flexible segment such as an alkyl or poly(oxyethylene) chain.[6] Therefore, the following reaction has been attempted: the combination of divinylbenzenes 1 with compounds 2 having two halophenyl groups that are connected to each other with a spacer chain.



Experimental Section

Materials. *m*- and *p*-divinylbenzene were prepared according to a reported method.[7] Monomers of **2a** (mp 87 °C from MeOH) and **2b** (mp 105 °C from $CHCl_3$–EtOH) were obtained by the reaction of 4-iodophenol with diethylene glycol bis(2-bromoethyl) ether and with 1,12-dibromododecane, respectively, according to a method described in the literature.[8] The monomers **2c** (mp 82 °C from $CHCl_3$) and **2e** (mp 70 °C from $CHCl_3$–EtOH) were prepared respectively by the reactions of 4-bromophenol with dodecanedioyl dichloride and of 4-iodobenzoyl chloride with 1,10-decanediol. Another monomer, **2d** (mp 58 °C from hexane), was prepared by the coupling reaction between 4-bromobenzyl bromide and hexamethylene bis(magnesium bromide) in the presence of dilithium tetrachlorocuprate as a catalyst.[9] Palladium acetate and tri-*o*-tolylphosphine (POT) were used without purification. DMF, pyridine, and tri-*n*-butylamine were distilled over CaH_2.

Polymerization. A typical procedure was as follows. To a solution of $Pd(OAc)_2$ (4.48 mg, 0.02 mmol), POT (12.2 mg, 0.04 mmol), and **2a** (0.598 g, 1 mmol) in 6 mL of DMF was added **1a** (0.130 g, 1 mmol) and tri-*n*-butylamine (0.740 g, 4 mmol) under Ar atmosphere. After 5 h at 100 °C, the reaction mixture was poured into 100 mL of MeOH. The precipitated polymer was filtered, washed with ether, and then dried in vacuo (a yellowish powder, 0.455 g). When the product polymer was soluble in an organic solvent, the polymer was purified by reprecipitation into ether after removal of the insoluble catalyst by filtration.

Measurement. ^1H NMR spectra were recorded on a JEOL GX-400 spectrometer (400 MHz). IR spectra were recorded on a Hitachi Model 260-50 infrared spectrophotometer. DSC analysis was carried out by employing a SEIKO DSC 200 (heating and cooling rate = 10 °C/min). All phase transition temperatures were read at the tops of the endothermic or exothermic peaks. A Nikon optical polarizing microscope equipped with a Mettler FP52 hot stage was employed for observation of thermal transition and anisotropic texture. TGA was carried out by employing a Shimazu TGC-30 (heating rate = 10 °C/min). Molecular weights of product polymers were estimated by GPC (polystyrene standards, $CHCl_3$ as an eluent, and Shodex A803 as a column). Intrinsic viscosity was measured by using the Ubbelohde viscometer.

Results and Discussion

Polycondensation. Polycondensation between equimolar amounts of 1 and 2 was carried out at 75–120 °C in DMF or pyridine in the presence of $Pd(OAc)_2/2POT$ as a catalyst and tri-*n*-butylamine as a base to produce

Table I
Polycondensation of 1 and 2 Catalyzed by the Palladium Complex[a]

								elemental analysis[e]		
run	monomers[b]	polymer	temp, °C	time, h	yield,[c] %	$\bar{M}_w$[d]	$\bar{M}_w/\bar{M}_n$[d]	C	H	Br or I
1	**1a, 2a**	PM1	100	5	94	14600	1.48	74.62 (74.27)	6.76 (6.73)	1.08 (1.29)
2	**1b, 2a**	PP1	100	4	99			72.23 (76.25)	6.49 (6.82)	2.74
3	**1a, 2b**	PM2	115	17	73			83.88 (84.96)	8.51 (8.39)	0
4	**1b, 2b**	PP2	100	5	96			76.59 (84.96)	7.68 (8.39)	8.71
5	**1a, 2c**	PM3	120	10	69	0.51[f]		74.98 (80.28)	7.13 (7.13)	3.31
6	**1b, 2c**	PP3	120	10	81			73.43 (80.28)	6.78 (7.13)	6.72
7	**1a, 2d**	PM4	120	10	69			86.62 (91.78)	7.95 (8.22)	3.43
8	**1b, 2d**	PP4	120	10	96			88.36 (91.78)	7.99 (8.22)	2.56

[a] In DMF or pyridine (run 3) containing $Pd(OAc)_2/2POT$ (2 mol % for **2** in runs 1–4, and 4 mol % for **2** in runs 5–8) and $(n\text{-}Bu)_3N$ (4 equivfor **2**). [b] [**1**] = [**2**] = 0.167 mol/L. [c] Calculated on the assumption that HX was released completely. [d] GPC (PSt standard; eluent, $CHCl_3$). [e] Calculated values are shown in parentheses. In run 1, the contents were calculated on the assumption that the one terminal of the polymer consisted of an iodophenyl group by using $\bar{M}_n$ values given by GPC. In all other cases, the values that were calculated without taking the polymer end groups into consideration are shown. [f] Intrinsic viscosity in *p*-chlorophenol/$CHCl_3$ (5/1 w/w) at 30 °C.

Table II
Polycondensation of 2e with and without 1 Catalyzed by the Palladium Complex[a]

										elemental analysis[f]		
run	monomers[b]	polymer	solvent	temp, °C	time, h	yield,[c] %	$\bar{M}_w$[d]	$\bar{M}_w/\bar{M}_n$[d]	$n/(m+n)$[e]	C	H	I
9	**1a, 2e**		pyridine	100	20	10	1400		0			
10	**1a, 2e**	PM5a	pyridine	115	10	54	6900	1.80	0	77.57 (77.62)	6.99 (6.89)	3.06 (3.31)
11	**1a, 2e**	PM5b	DMF	75	10	67	6580	1.61	0.37	79.16 (78.60)	7.14 (7.23)	0
12	**1a, 2e**	PM5c	DMF	100	5	70	6040	1.67	0.41	78.92 (78.46)	7.14 (7.25)	0
13	**1b, 2e**	PP5a	pyridine	115	17	80			0	77.85 (77.62)	7.01 (6.89)	1.30
14	**1b, 2e**	PP5b	DMF	100	5	87	0.19[g]		0.32	76.80 (77.62)	6.84 (6.89)	0.80
15	**2e**	P6	DMF	100	5	82	9100	1.83	0	74.81 (71.89)	7.48 (7.04)	0.59 (5.10)

[a] Catalyst, $Pd(OAc)_2/2POT$ (2 mol % for **2**); base, $(n\text{-}Bu)_3N$ (4 equiv for **2**). [b] [**1**] = [**2e**] = 0.167 mol/L. [c] Calculated on the assumption that HX was released completely. [d] GPC (PSt standard; eluent, $CHCl_3$). [e] The proportion of the biphenyl unit in the polymer, which is calculated on the basis of the ^{1}H NMR spectrum. [f] Calculated values are shown in parentheses. In runs 10 and 15, the contents were calculated on the assumption that the one (run 10) terminal or both (run 15) terminals of the polymer consisted of iodophenyl groups by using $\bar{M}_n$ values given by GPC. In runs 11 and 12, the calculated values are given on the basis of the polymer structure, which consists of biphenyl groups along with distyrylbenzene groups. In all other cases, the values that were calculated without taking the polymer end groups into consideration are shown. [g] Intrinsic viscosity in *p*-chlorophenol at 30 °C.

polymer **3** in good yield (Tables I and II). As the component of **2**, iodophenyl derivatives (**2a**, **2b**, and **2e**) were more reactive than bromophenyl derivatives (**2c** and **2d**), which reacted reasonably when more catalyst (4 mol % for **1**) was employed at a higher temperature, i.e., 120 °C. The polymerization proceeded homogeneously in runs 1, 5, 7, 9, 10, and 12, whereas in the other cases, product polymers precipitated during the reaction. Polymers derived from *p*-divinylbenzene with **2a–d** and those from *m*-divinylbenzene with **2b** and **2d** were mostly insoluble in common solvents, whereas the other polymers were soluble in organic solvents such as *p*-chlorophenol and $CF_3COOH-CHCl_3$. When the polymer was soluble in an organic solvent, the molecular weight was estimated by using GPC or the viscosity was measured.

The chemical structures of polymers have been established by spectroscopic methods as well as by elemental analyses. As examples, IR spectra of polymers PM4 and PP4 are shown in Figure 1. An absorption corresponding to an out-of-plane C–H bending vibration of a trans-1,2-disubstituted olefin is observed at 955 cm^{-1} (PM4) or at 965 cm^{-1} (PP4). Further support for these structures is obtained by ^{1}H NMR spectra of some polymer samples that are soluble in an organic solvent. Assignments of signals due to distyrylbenzene groups are summarized in Table III. The coupling constants of vinylene protons are in the range 15.95–16.40 Hz, which indicates the trans vinylene structure. These spectroscopic data have established the structures of product polymers that have *trans,trans*-distyrylbenzene groups in the main chains.

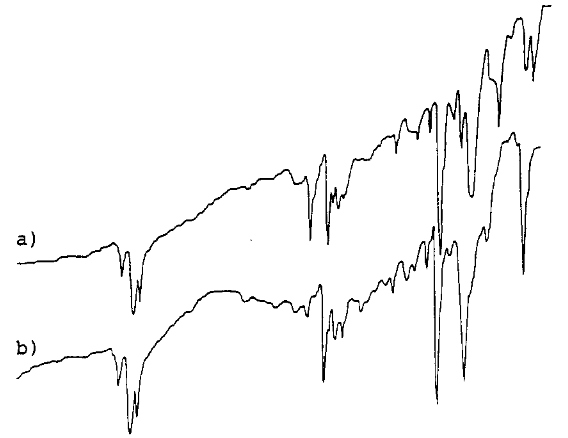
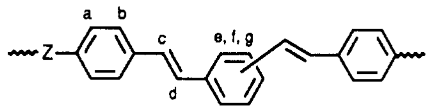


Figure 1. IR spectra (KBr) of the polymers: (a) PM4; (b) PP4.

^{1}H NMR spectra of the polymers, PM5b, PM5c, and PP5b, which were prepared by the reaction of **1** with *p*-iodobenzoate derivative **2e** in DMF, gave structural information for formation of biphenylene links in the polymers. In Figure 2b, which shows the ^{1}H NMR spectrum of PP5b, two doublet peaks are observed at δ 8.13 and 7.73 (*J* = 8.24 Hz) in addition to signals due to a distyrylbenzene unit and an unreacted iodophenyl group.[10] These peaks are assignable to the protons of a biphenyl group whose formation is ascribed to a palladium-catalyzed coupling reaction between two iodophenyl groups. The ratio of a biphenyl unit to a distyrylbenzene unit in the polymer chain has been calculated on the basis of the relative integral area of the corresponding proton signals (the value of $n/(m+n)$ in Table II). The content of the biphenyl unit is little influenced by the reaction temperature but dramatically changed due to the reaction solvent. In the ^{1}H NMR spectrum of the polymer PP5a produced

Table III
^{1}H NMR Spectra of Some of the Polymers



polymer	solvent	Z	a, b	c, d	e, f, g
PM1	$CDCl_3$	O	6.90 (d), 7.42 (d) J = 7.83 Hz	6.95 (d), 7.06 (d) J = 16.40 Hz	7.2-7.6 (m)
PM3	$CDCl_3/CF_3COOD$ (1/1 v/v)	CO_2	7.09 (d), 7.53 (d) J = 8.55 Hz	7.08 (d), 7.14 (d) J = 16.02 Hz	7.3-7.5 (m)
PM5a	$CDCl_3$	O_2C	7.59 (d), 8.04 (d) J = 7.80 Hz	7.16 (d), 7.23 (d) J = 15.65 Hz	7.3-7.5 (m)
PP5a	$CDCl_3/CF_3COOD$ (1/1 v/v)	O_2C	7.62 (d), 8.02 (d) J = 8.09 Hz	7.18 (d), 7.26 (d) J = 16.10 Hz	7.57 (s)

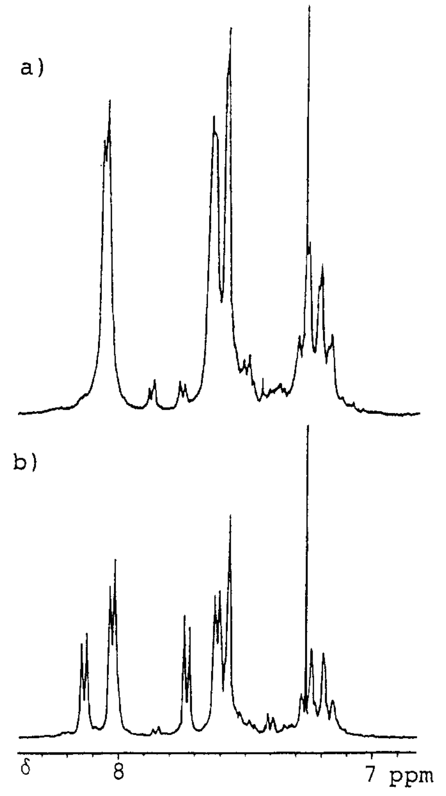
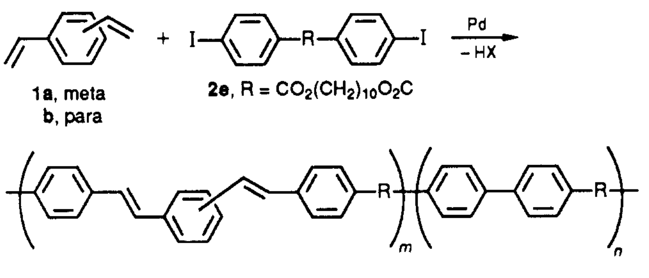


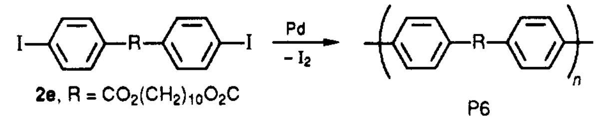
Figure 2. Lower field part of the expanded ^{1}H NMR spectra (400 MHz, in $CDCl_3/CF_3COOD$ (1/1 v/v)) of the polyesters: (a) PP5a prepared in pyridine; (b) PP5b prepared in DMF.



from the same monomers as PP5b, however, in pyridine, in which the polymerization proceeded more slowly than that in DMF, the peaks due to the biphenyl group are hardly observed (Figure 2a).[11]

It is of interest that the above phenyl-phenyl coupling reaction occurred only in the reaction involving **2e** in DMF. This coupling reaction between iodophenyl groups has been known to be favored in a polar solvent and by the presence of an electron-withdrawing group at the para position of the halogen atom.[12]

This observation prompted us to attempt the homopolycondensation of **2a** and **2e** without divinylbenzenes at 100 °C in DMF and in pyridine, respectively. Among four cases, only **2e** in DMF produced a polyester P6 having biphenyl groups (run 15 in Table II). This fact is taken to agree with the observation in the 1/**2e** polycondensation.



In Tables I and II, the calculated values of the elemental analysis for the polymers PM1, PM5a, and P6 have been estimated on the assumption that the one terminal (PM1 and PM5a) or both terminals (P6) of the polymers consist of iodophenyl groups by using the $\bar{M}_n$ values given by GPC. The calculated values in PM1 and PM5a agree with the found ones. On the other hand, in the polymer P6, the found value of iodine is smaller than the calculated one. This is probably caused by the dehalogenation, which is known as another side reaction in the Heck reaction. Moreover, nondetection of iodine in the polymers PM2, PM5b, and PM5c is due to the coupling reaction between two iodophenyl groups and due to the dehalogenation. Especially, as mentioned above for PM5b and PM5c, the frequent occurrence of the coupling reaction has been indicated also by the ^{1}H NMR spectra.

Thermal Behavior (Table IV). The Polymers of the PM Series. The polyethers and polyesters of the PM series, which were derived from *m*-divinylbenzene, except for polyhydrocarbon PM4 ($T_m = T_i$) clearly showed liquid crystallinity. Endothermic peaks on their DSC thermograms and characteristic textures of their mesophases through the polarizing microscope were observed.

As an example, Figure 3 shows the thermograms of the polyester PM3. On the first heating scan (line a), three overlapping endothermic transitions were observed, which were separated into four endothermic peaks on the second heating scan (line c). Polarizing microscopy indicated that the first peak and the last one were due to a solid-liquid crystal transition and a liquid crystal-isotropic liquid one, respectively. The mesophases of PM3 showed smetic liquid crystallinity, which was characterized by the following observation through the polarizing microscope; on the cooling scan from the isotropic state, bâtonets began to appear on the dark background at 175 °C, growing up gradually, and finally a fan-shape texture was observed (Figure 4).

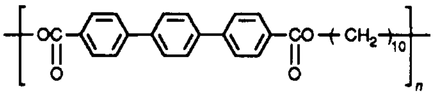
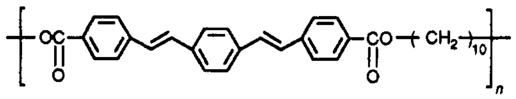
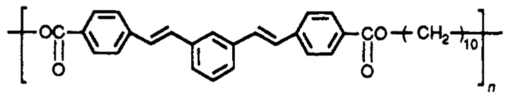
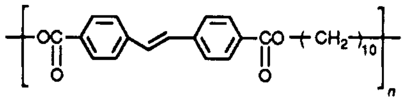
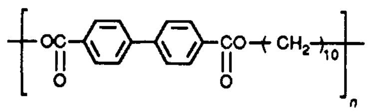
A mesophase of the polyester PM5a, whose ester groups linking a mesogen to a spacer have the reverse orientation of those in PM3, was observed in a narrower range of temperature, i.e., between 155 and 164 °C, than that

Table IV
Thermal Behavior of the Polymers

polymer	phase transition temp, °C[a] T_m	T_1	T_2	T_i	TGA, °C[b] T_s	T_1	T_5
PM1	132			167	230	295	365
PP1	(200)			(285)	250	280	312
PM2	131	177		195	238	370	405
PP2	179			(240)	233	287	308
PM3	123	157	171	184	185	232	310
PP3	(240)				223	262	315
PM4	195 (=T_i)				243	313	402
PP4					242	305	402
PM5a	155			(164)	240	320	362
PM5b	103	110	122	129	265	340	385
PP5a	218			(275)	303	326	355
PP5b	136	158		(250)	320	358	380
P6	145	152		158	205	320	375

[a] T_m is the temperature of a solid–mesophase transition. T_1 and T_2 are temperatures of transitions between mesophases. T_i is the temperature of a transition to an isotropic liquid. Values without parentheses are given by the DSC measurement (heating rate = 10 °C/min) on the first heating scans (PP5a and PP5b) or on the second heating scans (the polymers of PM-series and P6). On the other hand, values in parentheses are given by the polarizing microscopic observation. [b] T_s is the temperature at which the weight loss of the polymer starts. T_1 and T_5 are temperatures at which 1% and 5% of the polymer's weight is lost, respectively. TGA was carried out under a nitrogen atmosphere with a heating rate of 10 °C/min.

Table V
Thermal Behavior of the LC Polyesters Consisting of Different Mesogens with the Same Flexible Chain

	polyesters	phase transition temp, °C[a] T_m	T_i	ΔT
P7[b]		256	311	55
PP5a		218	275	57
PM5a		155	164	9
P8[b]		197	200	3
P6		145 (151)[c]	158 (161)[c]	13

[a] T_m = solid–mesophase transition, T_i = mesophase–isotropic liquid transition, $\Delta T = T_i - T_m$. [b] Data from ref 16. [c] Data from ref 15.

of PM3.[13] It showed a fine graining view, which was also observed in mesophases of PM1 and PM2, through the polarizing microscope (Figure 5).

The Polymers of the PP Series. The polymers of the PP series, which were derived from *p*-divinylbenzene, showed higher phase transition temperatures than those of the PM series. In the case of PP3 and PP4,[14] the thermal degradation started before the phase transition. Since the relatively high temperature induced cross-linking reactions of the polymers (see below), peaks due to some phase transitions were not observed clearly on DSC thermograms (heating rate of 10 °C/min). However, on rapid heating, a highly viscous birefringent liquid was observed as a mesophase through the polarizing microscope (the transition temperatures are shown in the parentheses in Table IV). Increasing the temperature did not induce a transition to an isotropic state but made the birefringence dull and the polymer solidified. This behavior of the polymers of the PP series is due to a thermal cross-linking reaction, since the polymer became insoluble in any solvents after it was heated.

In the DSC curves of PP3, only one endothermic peak was observed at 194 °C on the first scan, which was ascribed to a solid–solid transition but not to a solid–mesophase one on the basis of observations with the polarizing microscopy. On cooling and reheating, however, no peak appeared.

A copolymer of PM5b and PP5b that had biphenyl groups along with distyrylbenzene groups as mesogens showed lower phase transition temperatures than the related polyesters PM5a and PP5a. The thermal behavior of the polymer P6, which consisted of a biphenyl group as a mesogenic one, was similar to that of the structurally related polymer prepared previously in another way.[15]

Table V shows the contrast among the thermal behaviors of LC polyesters that have been synthesized previously as well as those described in this article. These

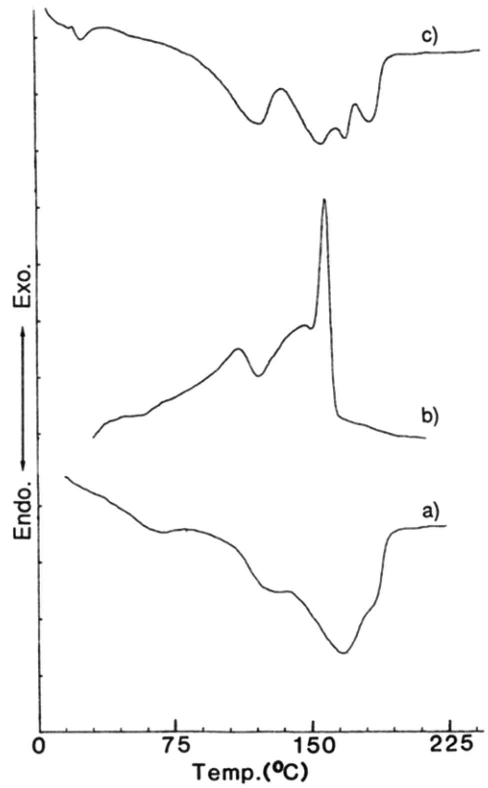


Figure 3. DSC thermograms (heating and cooling rates = 10 °C/min) of the polyester PM3: (a) the first heating scan; (b) the cooling scan; (c) the second heating scan.

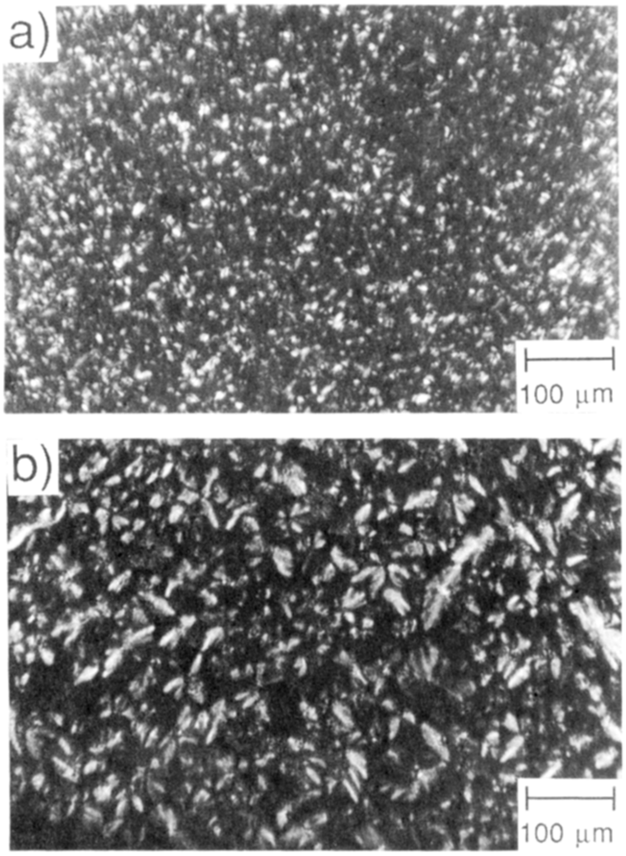


Figure 4. Photographs through the cross-polarizing optical microscope of the polyester PM3 at 175 °C (a) and at 130 °C (b) on cooling.

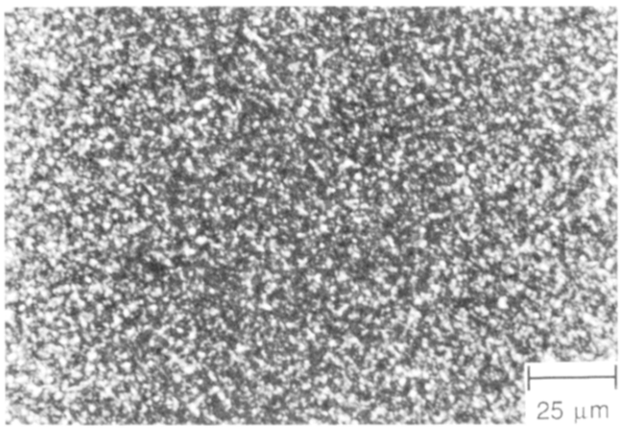


Figure 5. Photograph taken with a cross-polarizing optical microscope of the polyester PM5b at 159 °C on reheating.

polyesters consist of different mesogens with the same flexible chain, i.e., decamethylene. In this case, characteristics such as rigidity, linearity, and length of the mesogens determine the thermal behavior of the polymer.[16] The *trans,trans-p*-distyrylbenzene moiety, which is the longest but less rigid than the terphenyl moiety, provides as large a ΔT value as the terphenyl one (P7). It is, however, much larger than the ΔT value of P8, incorporating the *trans*-stilbene moiety. On the other hand, for T_m and T_i the order is P7 > PP5a > P8. On the contrary, the *trans,trans-m*-distyrylbenzene moiety, which has the lowest linearity, causes the T_m to be much lower and the ΔT value to be a little larger than those of P8.

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Radical Copolymerization of Lipoamide with Vinyl Monomers

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ABSTRACT: Lipoamide, which is a five-membered cyclic disulfide, was copolymerized with some vinyl monomers (styrene, vinyl acetate, acrylonitrile, and methyl acrylate) by 2,2′-azobis(isobutyronitrile) as a radical initiator at 82 °C for 2 h in benzene to give copolymers with sulfide linkages in the main chain and various functional groups as pendants in good yield. The copolymerization might proceed by chain-transfer-type attacking of the propagating vinyl polymer radical at the S–S bond of lipoamide.

Introduction

Lipoamide (LAm), a five-membered cyclic disulfide, works as a coenzyme in the oxidative acyl transfer reaction in living systems. We have already investigated the application of its acyl transfer and redox character to organic synthesis.[1,2]

On the other hand, cyclic disulfides copolymerize with vinyl monomers by homolytic reactions. For example, styrene[3] and vinyl acetate[4] copolymerize with 1-oxa-3,4-dithiacycloheptane (a seven-membered cyclic disulfide) by chain transfer of their propagating polymer radicals to cyclic disulfides to give polymers with sulfide linkages in the main chain. By ultraviolet irradiation, a disulfide linkage of trimethylene disulfide (a five-membered cyclic disulfide) is cleaved to form thiyl radicals and polymerized.[5] Then cyclic disulfides are attractive as comonomers in radical polymerization. We have already reported thermal and photoinitiated copolymerization of LAm with styrene without initiators.[6]

In this paper, we describe the copolymerization of LAm, which is a cyclic disulfide having an amide group, with vinyl monomers, i.e., styrene (St), methyl methacrylate (MMA), vinyl acetate (VAc), acrylonitrile (AN), and methyl acrylate (MA), in the presence of 2,2′-azobis(isobutyronitrile) as a radical initiator. For comparison, we report the synthesis of 4,4′-bis[(benzoyloxy)methyl]-1,2-dithiolane (BDT), which is a five-membered cyclic disulfide without an amide group, and its copolymerization with styrene.

Experimental Section

Materials. Lipoamide (LAm) was supplied by Fujisawa pharmaceutical Co. Ltd. and recrystallized from acetonitrile. Vinyl monomers and solvents were purified by the usual procedure.

Measurements. IR spectra were recorded on a JASCO FT/IR-3 spectrophotometer. ^{1}H NMR spectra were recorded on a JNM-FX 100 FT NMR and a JEOL PMX-60 spectrometer. GPC measurement of polymers in tetrahydrofuran (THF) was carried out with a TOYO SODA HPLC CCCP&8000 system equipped with polystyrene gel columns (TSK gel G2000H, G2500H, and G3000H). The number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$) were calculated on the basis of polystyrene.

Copolymerization of LAm with Vinyl Monomers. Typical procedure: LAm (0.306 g, 1.49 mmol), St (0.879 g, 8.44 mmol), 2,2′-azobis(isobutyronitrile) (AIBN) (32.6 mg, 0.199 mmol), and dimethyl sulfoxide (DMSO) (2.34 mL) were charged into a Pyrex tube and the solution was degassed. The copolymerization was carried out in a sealed tube at 82 °C for 2 h with stirring. After the reaction, the reaction solution was diluted with chloroform and the polymer was precipitated with methanol, separated by filtration, and dried in vacuo. A white powdery copolymer was obtained (0.586 g, 49.4%). ^{1}H NMR ($CDCl_3$) δ 0.8–3.0 (CH_2, CH), 3.3 (CHS), 5.3 ($CONH_2$), and 6.3–7.4 ppm (Ph); IR (KBr) 3400, 3500 (NH_2), 1674 ($CONH_2$), 1602, 1494, and 698 cm^{-1} (Ph). The content of LAm in the copolymer was estimated by ^{1}H NMR to be 7.8 mol %.

The copolymerization of LAm with other comonomers was carried out by the same procedure as above.

When MMA was used as a comonomer, the copolymerization did not proceed and homopolymer of MMA alone was obtained.

When MA was used as a comonomer, the resulting copolymer was precipitated with ether, separated by decantation, and dried in vacuo to obtain a colorless viscous polymer in 88.4% yield. The content of LAm, 11.9 mol %; ^{1}H NMR ($CDCl_3$) δ 1.0–2.6 (CH_2, CH), 2.7 (CHS), 3.7 (CH_3), and 5.8 ppm ($CONH_2$); IR (KBr) 3200, 3370 ($CONH_2$), 1740 (COO), 1660, 1630 ($CONH_2$), and 1166 cm^{-1} ($COOCH_3$).

When VAc was used as a comonomer, a colorless viscous copolymer was obtained in 77.7% yield. ^{1}H NMR ($CDCl_3$) δ 1.2–2.3 (CH_2), 2.0 (CH_3), 2.5–3.1 (CHS, SCH_2), 4.9 (CHO), and 6.0 ppm ($CONH_2$); IR (KBr) 3450 (NH_2), 1740 (COO), 1668, 1628 ($CONH_2$), and 1240 cm^{-1} (CH_3COO).

When AN was used as a comonomer, the reaction solution was diluted with *N,N*-dimethylformamide (DMF) and the resulting copolymer was precipitated with methanol, separated by

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