CHEMISTRY LETTERS, pp. 557-560, 1994.

Synthesis and Copolymerization of a Mesogenic Acrylate Having 4-(2,2,6,6-Tetramethylpiperidyl-4-oxy)phenyl Benzoate as a Precursor for Nitroxide-Containing Liquid-Crystalline Side-Chain Polymers

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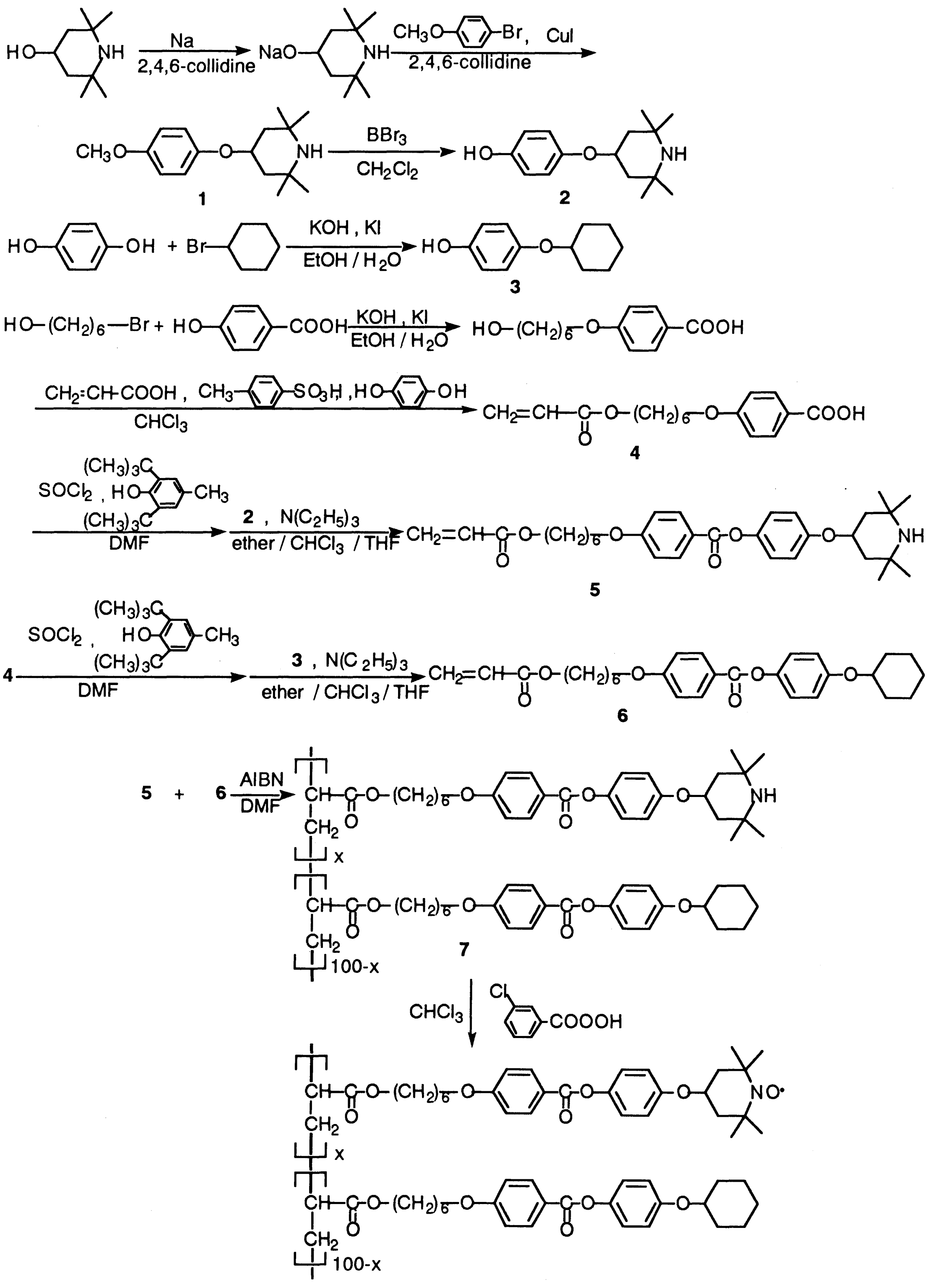
A mesogenic acrylate monomer 4-(2,2,6,6-tetramethylpiperidyl-4-oxy)phenyl 4'-(6-acryloyloxyhexyl)benzoate was synthesized and copolymerized with 4-cyclohexyloxyphenyl 4'-(6-acryloyloxyhexyloxy)benzoate. Oxidation of the copolymer yielded a nitroxide-containing liquid-crystalline side-chain polymer.

In recent years, considerable interest has been directed to side-chain liquid-crystalline (LC) polymers¹⁾ with functional groups incorporated in their side-chains.2) Incorporation of nitroxide radicals into the side-chain LC polymers is interesting for the following two reasons. Firstly, a small number of nitroxide radicals covalently incorporated into an LC phase can serve as spin labels and their ESR spectra can provide information on local motions of mesogens in various mesophases.3a,b) Secondly, if a large number of nitroxide radicals are incorporated into an LC phase, the radical spins can be aligned in LC order, which may lead to a radical spin cluster system worth studying from a point of view of molecular-based magnetic materials.4a,b)

In the present study, we synthesized a mesogenic acrylate monomer having 4-(2,2,6,6-tetramethylpiperidyl-4-oxy)phenyl benzoate as a precursor for the mesogenic nitroxide radical, and the precursor monomer was copolymerized with a mesogenic acrylate comonomer based on 4-cyclohexyloxyphenyl benzoate. The 4-cyclohexyloxyphenyl benzoate group was chosen as the mesogenic group for the comonomer because of a reasonable degree of structural similarity between these two types of the mesogenic groups, which allows the mesogens to accommodate each other in an LC phase.

The syntheses of the mesogenic acrylates were performed via Scheme 1. 4-Methoxyphenyl 2,2,6,6-tetramethyl-4-piperidyl ether (**1**)5) was synthesized by treating 2,2,6,6-tetramethyl-4-piperidinol with Na in 2,4,6-collidine followed by coupling with *p*-bromoanisole in the presence of a catalytic amount of CuI. 4-Hydroxyphenyl 2,2,6,6-tetramethyl-4-piperidyl ether (**2**)6) was prepared by treating **1** with BBr_3 in 1,2-dichloroethane. 4-Hydroxyphenyl cyclohexyl ether (**3**)7) was prepared by coupling *p*-hydroquinone with cyclohexyl bromide in the presence of KOH. 4-(6-Acryloyloxyhexyloxy)benzoic acid (**4**)8) was synthesized according to the literature9) with some modifications. Compound **4** was coupled with **2** via an ester linkage to give 4-(2,2,6,6-tetramethylpiperidyl-4-oxy)phenyl 4'-(6-acryloyloxyhexyl)benzoate (**5**).10) 4-Cyclohexyloxyphenyl 4'-(6-acryloyloxyhexyloxy)benzoate (**6**)11) was synthesized from **3** and **4** in a manner analogous to the synthesis of **5**. The chemical structures of all the products were verified with NMR spectroscopy, mass spectrometry, and elemental analysis. Monomer **5** was found to form an LC phase with transitions from a crystalline to LC and from LC to isotropic phase at 148.5 °C and at 175.3 °C, respectively. On the other hand, monomer **6** showed no LC phase with only a transition from a crystalline to isotropic phase at 58.5 °C.



Scheme 1.

Monomer **6** was copolymerized with 1 mol% of **5** in the presence of 2,2′-azobisisobutyronirile (AIBN) in DMF at 60 °C for 20 h to give the copolymer (**7**).12) Copolymer **7** was then oxidized by treating with *m*-chloroperbenzoic acid in chloroform at room temperature to convert the 2,2,6,6-tetramethylpiperidine groups into nitroxide radicals. An ESR spectrum of a dilute chloroform solution of the oxidized copolymer indicated the formation of the nitroxide radicals. As shown in Fig.1, the nitroxides in the oxidized copolymer gave an ESR spectrum of an unsynmetrically broadened three-line pattern typical of moderately restricted motions.[3a,b)]

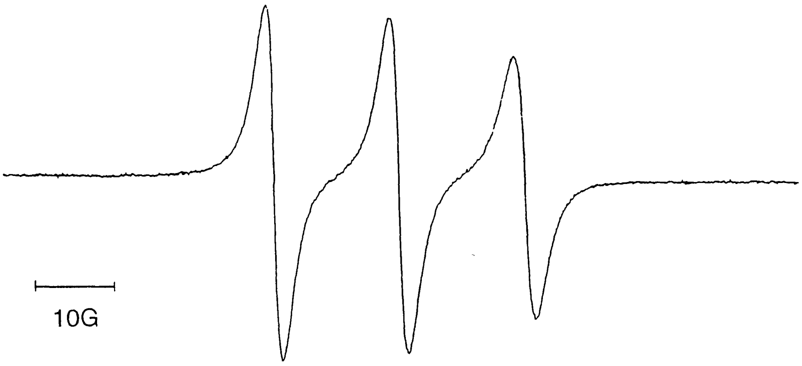


Fig. 1. ESR spectrum of a dilute chloroform solution of copolymer **7** oxidized by *m*-chloroperbenzoic acid.

Thermal phase transition temperatures of copolymer **7** were determined with a differential scanning calorimeter (Seiko Instruments SSC 5200H) at a scan rate of 5 °C/min. Prior to measurement, the sample was heated to a temperature 30 °C higher than the isotropization temperature and gradually cooled down to room temperature for annealing. Figure 2 shows a DSC thermogram observed for copolymer **7** on heating. The copolymer showed a glass transition temperature (T_g) at 33 °C and two endothermal peaks probably corresponding to the transition from a smectic to nematic mesophase at 56 °C and that from the nematic to isotropic phase at 71 °C. Under a polarizing microscope, birefringence was observed below the isopropization temperature, but the textures have yet to be defined carefully.

Further detailed studies of the spin-labeled side-chain LC copolymer by ESR are now under way in our laboratory. We are also working on the synthesis of the side-chain LC polymers with a high content of the nitroxide radical, and investigating magnetic interactions of the radical spins aligned in LC order. The results of these studies will be reported in subsequent papers.

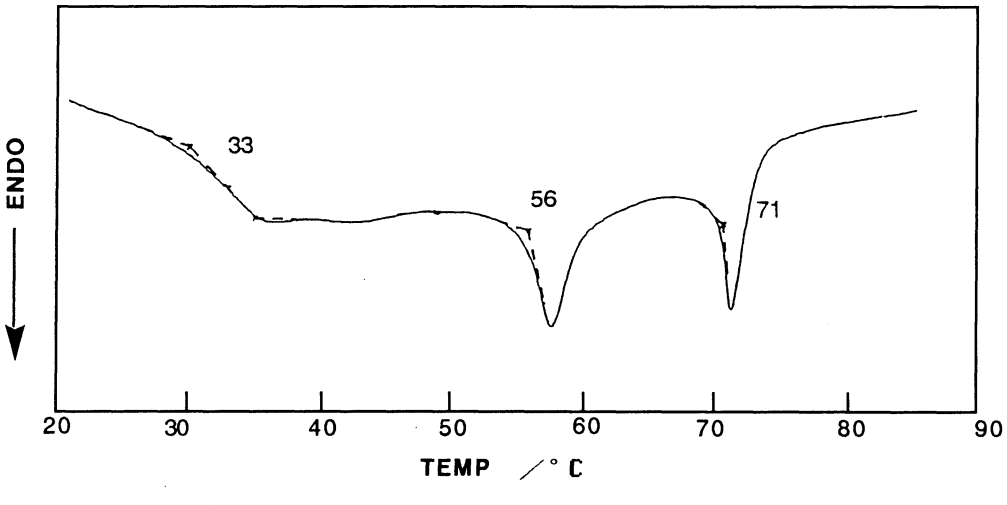


Fig. 2. DSC thermogram of copolymer **7** upon heating.

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (004) from the Ministry of Education, Science, and Culture, Japan.

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5) Compound **1**: 17.1% yield; yellow oil; ^{1}H NMR (270 MHz, DMSO-d_6) δ 8.89(s, 1H), 6.77(d, 2H), 6.66(d, 2H), 4.48(m, 1H), 1.88(m, 2H), 1.16(s, 6H), 1.08(m, 2H), 1.04(s, 6H).

6) Compound **2**: 39.4% yield; white needles; mp 198-200 °C; ^{1}H NMR (270 MHz, CDCl$_3$) d 6.88(s, 4H), 4.50(m, 1H), 3.77(s, 3H), 2.10(m, 2H), 1.86(m, 2H), 1.67(s, 6H), 1.56(s, 6H).

7) Compound **3**: 17.0% yield; brown oil; ^{1}H NMR (270 MHz, CDCl$_3$) d 6.82(d, 2H), 6.73(d, 2H), 4.73(s, 1H), 4.08(m, 1H), 1.97(m, 2H), 1.78(m, 2H), 1.58-1.28(m, 6H).

8) Compound **4**: 53.0% yield; white needles; mp 101-102 °C; ^{1}H NMR (270 MHz, DMSO-d_6) d 7.87(d, 2H), 6.99(d, 2H), 6.32(d, 1H), 6.14(q, 1H), 5.88(d, 1H), 4.02(m, 4H), 1.66-1.40(m, 8H).

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10) Compound **5**: 14.2% yield; white needles; mp 148.5 °C; ^{1}H NMR (270 MHz, CDCl$_3$) d 8.14(d, 2H), 7.14(d, 2H), 6.95(m, 4H), 6.42(d, 1H), 6.14(q, 1H), 5.83(d, 1H), 4.67(m, 1H), 4.19(t, 2H), 4.04(t, 2H), 2.14(m, 2H), 1.88-1.42(m, 20H); MS m/z 523(M$^+$).

11) Compound **6**: 22.6% yield; white needles; mp 58.5 °C; ^{1}H NMR (270 MHz, CDCl$_3$) d 8.14(d, 2H), 7.11(d, 2H), 6.95(m, 4H), 6.42(d, 1H), 6.16(q, 1H), 5.83(d, 1H), 4.19(m, 3H), 4.03(t, 2H), 2.00-1.31(m, 18H); Anal. Found: C, 71.71; H, 7.38%. Calcd for $C_{28}H_{34}O_6$: C, 72.08; H, 7.35%.

12) Copolymer **7**: Purified by reprecipitation from a chloroform solution into ether; 14% yield (on the basis of the total monomers); Weight-average molecular weight (Mw)(GPC with THF) 1.2x10^4 (calibrated with standard polystyrenes), Mw/Mn 1.5.

(Received December 1, 1993)