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## Liquid Crystals

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Xi Zhang

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# Preliminary communication

## Liquid crystalline polyacrylates using hyperbranched poly(*p*-chloromethylstyrene) as initiator

XI ZHANG, YONGMING CHEN, AIJUN GONG, CHUANFU CHEN  
and FU XI\*

Polymer Chemistry Laboratory, Chinese Academy of Sciences and  
China Petro-chemical Corporation, Institute of Chemistry,  
Chinese Academy of Sciences, PO Box 2709, Beijing 100080, PR China

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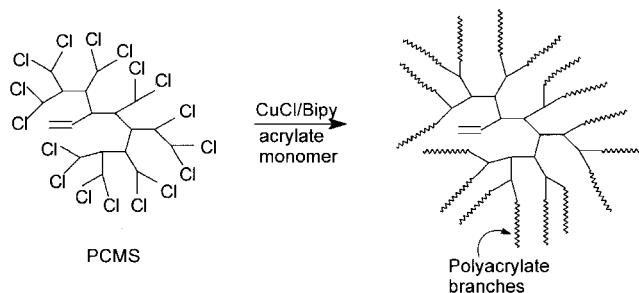
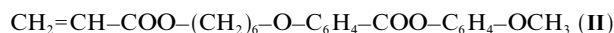
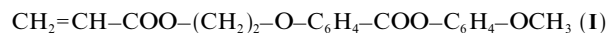
Two kinds of acrylate monomers, i.e. 4-methoxyphenyl 4-{{2-(1-oxo-2-propenyloxy)ethyl}oxy}-benzoate (I) and 4-methoxyphenyl 4-{{6-(1-oxo-2-propenyloxy)hexyl}oxy}benzoate (II) were polymerized using hyperbranched poly(*p*-chloromethylstyrene) (PCMS) as an initiator by atom transfer radical polymerization (ATRP). The resulting dendritic graft copolymers were characterized by means of gel permeation chromatography, differential scanning calorimetry, and polarization microscopy. The mesophase behaviour of these dendritic copolymers essentially depends on the chemical nature of the polyacrylates.

Dendritic polymers have received much attention in the last few years [1, 2] since Tomalia *et al.* [3, 4] reported the preparation of poly(amidoamine) dendrimer. These polymers can be divided into two kinds: dendrimers and hyperbranched polymers. Emphasis has recently shifted from the mere construction of (macro)molecules with dendritic topology to materials with specific functions and exhibiting intriguing supramolecular organizational phenomena [5]. Percec *et al.* [6] reported the first spherical supramolecular dendrimers, self-organized in a novel thermotropic cubic liquid crystalline phase; Frey *et al.* [5] and Shibaev *et al.* [7] reported the functionalization of carbosilane dendrimers with rigid mesogenic units on the surface.

It is well known that 'living' atom transfer radical polymerization (ATRP) has aroused wide interest, and Fréchet *et al.* [8] successfully prepared dendritic graft copolymers by the ATRP method. Obviously, this complex architecture might be useful for the preparation of advanced materials with new and/or improved properties.

In this paper, we report the polymerization of two kinds of acrylate monomers, i.e. 4-methoxyphenyl 4-{{2-(1-oxo-2-propenyloxy)ethyl}oxy}benzoate (I) and 4-methoxyphenyl 4-{{6-(1-oxo-2-propenyloxy)hexyl}oxy}benzoate (II), using hyperbranched poly(*p*-chloromethylstyrene) (PCMS) as a multicentre initiator by ATRP. The resulting polymers were characterized by means

of gel-permeation chromatography (GPC), differential scanning calorimetry (DSC) and polarization microscopy.



Scheme.

The hyperbranched liquid crystalline copolymer is shown in the scheme. The hyperbranched liquid crystalline polymer obtained is considered as a novel graft copolymer. It consists of the internal core which is a hyperbranched non-mesogenic block and the outside layer which is a mesogenic block. This liquid crystalline polymer with its new structure might possess some potential advantages as a result of its hyperbranched topology, such as low viscosity.

For the synthesis, *p*-xylene was purified in the usual manner and distilled over sodium before use. The monomers I and II were prepared according to the

\* Author for correspondence.

literature [9]. The elemental analysis and  $^1\text{H}$  NMR data were consistent with the expected structures. The hyperbranched PCMS was prepared according to the procedure of Matyjaszewski [10]. The  $M_n$  of the PCMS is 2532 by  $^1\text{H}$  NMR and 2361 by GPC; the polydispersity is 2.5. Per molecule of PCMS there are 16.6 chloromethyl groups, i.e. initiating sites, on average.

The polymerizations were carried out using 50% (w/v) solutions of monomer in *p*-xylene at 120°C under a nitrogen atmosphere. The ratio of the molar equivalents of PCMS:CuCl<sub>2</sub>:2,2'-bipyridyl was 1:1:3. After the appropriate time the reaction mixture was dissolved in CHCl<sub>3</sub> and the solution filtered through a short plug of alumina; concentration under vacuum and precipitation by addition of ether gave the polymers as white solids.

Gel permeation chromatography (Waters 510) measurements were carried out with tetrahydrofuran as solvent, and the molecular mass was calculated relative to standard polystyrene. The DSC measurements were carried out using a Perkin-Elmer 7 series thermal analysis system with a heating rate of 20°C min<sup>-1</sup>. Mesomorphic behaviour was investigated by polarization microscopy using a Leitz model Laborlux 12 Pol microscope.

Table 1 shows the results of polymerization of the acrylate monomers. According to Fréchet's report [8], the presence of a large number of radical centres in the same macromolecule greatly increases the possibility of crosslinking in dendritic polymers. They used the core polymer with an average of 37.8 initiating sites per molecule to initiate the polymerization of styrene and *n*-butyl methacrylate at 115°C. The molar fraction of the core polymer was 0.5% and the time of polymerization was usually not more than 28 h. When the polymerization was conducted at higher temperatures and for extended times, insoluble crosslinked materials formed in every case. In our case, we used the core polymer with an average of 16.6 initiating sites per molecule to initiate the polymerization at 120°C. No insoluble crosslinked materials were found even though the molar fraction of PCMS was as large as 5% and the time of polymerization was as long as 120 h. The assumed reason is that the two kinds of acrylate monomer used here possess lower reactivity in polymerization than styrene and *n*-butyl methacrylate.

The  $M_w$  of the polymers were determined by GPC. It should be noted that this method gives a low estimate of the actual molecular mass due to the star-like nature of the polymers [11]. From the  $M_w$  and  $M_w/M_n$  values in table 1, the  $M_n$  values for the polymers can be obtained, and compared with the  $M_n$  results of Ringsdorf *et al.* [9] obtained by vapour phase osmometry; the dendritic graft copolymers have higher  $M_n$  than that of the linear polyacrylate using the same molar fraction of initiator. This is due to the many initiating sites of the core polymer. The yield of polymer **I** is greater than that of polymer **II** because the longer spacer chain increases the difficulty of polymerization of the monomer.

The structures of **Ic** and **IIb** were confirmed by  $^1\text{H}$  NMR. For **Ic**:  $^1\text{H}$  NMR (CDCl<sub>3</sub>): 1.2–2.0 (2H, –CH<sub>2</sub>–), 2.2–2.7 (1H, –CH–C=O), 3.4–3.9 (3H, –OCH<sub>3</sub>), 3.9–4.6 (4H, –CH<sub>2</sub>–O–, O=C–O–CH<sub>2</sub>–), 6.6–7.2 (6H, PhH–O–), 7.7–8.3 (2H, PhH–C=O). For **IIb**:  $^1\text{H}$  NMR (CDCl<sub>3</sub>): 1.2–2.0 (10H, –CH<sub>2</sub>–, –(CH<sub>2</sub>)<sub>4</sub>–), 2.1–2.5 (1H, –CH–C=O), 3.5–4.3 (7H, –OCH<sub>3</sub>, –OCH<sub>2</sub>–), 6.6–7.2 (6H, PhH–O–), 7.8–8.4 (2H, PhH–C=O). The  $^1\text{H}$  NMR spectra did not show peaks for the PCMS core because the amount of PCMS in the copolymer is quite small.

The phase behaviour of these graft copolymers generally depends on the chemical nature of the polyacrylate branches. This fact is in agreement with the view that many of the properties of dendrimers are determined mainly by the chemical nature of the surface groups [12].

Table 2 summarizes the phase transition temperatures and transition enthalpies of polymers **Ia–IIb**. According to Ringsdorf's report [9], the liquid crystalline phase range is widened by increasing the molecular mass; this is also true in our cases. For example, because the average molecular mass of polymer **Ia** is greater than that of polymer **Ic**, the nematic phase of **Ia** has a broader range than **Ic** and the clearing point of **Ia** is higher than that of **Ic**. The phase transition temperatures of the dendrigraft copolymers were similar to those of linear polyacrylates, showing that phase transition temperatures appear to reach a plateau after the molecular mass reaches a certain value [9].

Table 1. Polymerization of acrylate monomers with PCMS as the initiator in *p*-xylene at 120°C.

Polymer	Monomer	Mol% of PCMS	Time/h	Yield/%	$M_w$ ( $\times 10^{-4}$ )	$M_w/M_n$
<b>Ia</b>	<b>I</b>	1	72	58	10.7	3.35
<b>Ib</b>	<b>I</b>	2	26	71	7.3	3.82
<b>Ic</b>	<b>I</b>	5	26	75	7.2	5.56
<b>IIa</b>	<b>II</b>	2	120	20	8.0	3.11
<b>IIb</b>	<b>II</b>	5	48	50	8.3	5.36

Table 2. Phase transition temperatures and transition enthalpies of the polymers; g=glass, Sm=smectic, N=nematic, I=isotropic;  $\Delta H(\text{Sm-N})$ =transition enthalpy for the transition smectic–nematic;  $\Delta H(\text{N-I})$ =transition enthalpy for the transition nematic–isotropic.

Polymer	Phase transition/ $^{\circ}\text{C}$	$\Delta H(\text{Sm-N})/\text{kJ mol}^{-1}$	$\Delta H(\text{N-I})/\text{kJ mol}^{-1}$
<b>Ia</b>	g 62 N 113 I	—	0.53
<b>Ib</b>	g 64 N 113 I	—	0.76
<b>Ic</b>	g 62 N 107 I	—	0.68
<b>IIa</b>	g 29 Sm 84 N 111 I	1.19	0.78
<b>IIb</b>	g 32 Sm 89 N 120 I	0.74	0.81

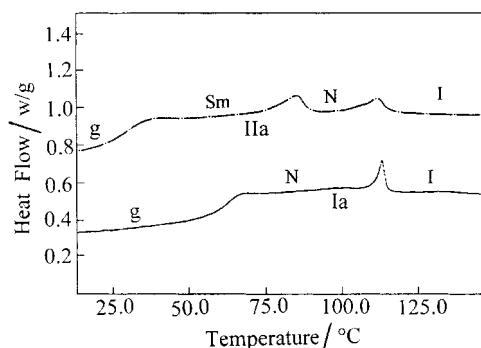


Figure 1. DSC heating curves for polymer **Ic** and polymer **IIb** (heating rate  $20^{\circ}\text{C min}^{-1}$ ); g=glassy liquid crystal, Sm=smectic melt, N=nematic melt, I=isotropic melt.

Figure 1 shows the DSC heating curves of polymer **Ia** and polymer **IIa**. For polymer **Ia**, the glass transition is observed at  $62^{\circ}\text{C}$ . Above this temperature, polymer **Ia** forms a nematic phase. The endotherm at  $113^{\circ}\text{C}$  is due to isotropization. For polymer **IIa**, a smectic phase and a nematic phase were observed. The  $T_g$  of the PCMS core itself was measured as  $48^{\circ}\text{C}$ , but it could not be seen in the DSC curves due to the small amount of PCMS contained in the copolymers.

Polymer **IIb** was investigated by polarization microscopy. Upon cooling from the isotropic phase, similar schlieren textures were observed (figure 2) at both  $105^{\circ}\text{C}$  and  $70^{\circ}\text{C}$  for the N and SmC phases, respectively.

In conclusion, liquid crystalline dendritic copolymers have been prepared using hyperbranched PCMS as the initiator by atom transfer radical polymerization. The phase behaviour of the copolymers essentially depends on the chemical nature of the grafted polyacrylates and is similar to that of the linear analogues prepared by Ringsdorf *et al.* [9]. It seems that the hyperbranched structure of the copolymers obtained has not had an obvious influence on the liquid crystalline properties.

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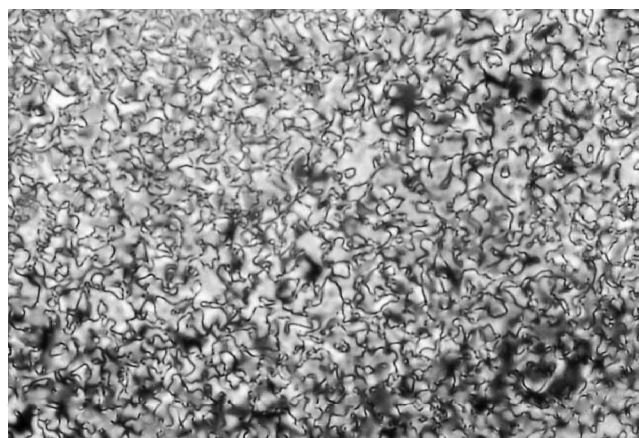


Figure 2. Optical polarizing photomicrograph of the schlieren texture of the SmC phase ( $70^{\circ}\text{C}$ , magnification  $\times 320$ ) for polymer **IIb**. The nematic phase has a similar schlieren texture.

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