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Side chain liquid crystalline polyether macromonomers and their polymerization

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SUMMARY

Cationic polymerization of mesogenic epoxides using hydroxyethyl methacrylate/BF3 as the initiator system led to novel polyether macromonomers bearing a methacrylate functionality. These macromonomers exhibited nematic or smectic mesophases depending on the length of the alkoxy tail of the aromatic mesogen. Low molar mass polymers obtained from these macromonomers showed the same type of mesophases. However, with a high molar mass polymer a change from smectic to nematic was found.

INTRODUCTION

The synthesis of macromonomers with methacrylic end groups by cationic polymerization of propylene oxide and epichlorohydrin in the presence of hydroxyethyl methacrylate (HEMA) has been reported (BRZEZINSKA and KUBISA 1989). According to the "activated monomer" mechanism (PENCZEK et al. 1986), the molar mass of the resulting polyether could be controlled by the ratio [epoxy monomer]:[alcohol] and little or no cyclic oligomers were found.

We have applied this type of cationic polymerization to epoxy monomers Ia and Ib, containing mesogenic groups to prepare macromonomers with polyether chains of varying length and consequently a varying number of mesogenic side groups (IIa, IIb).

By polymerization of these macromonomers, grafts of liquid crystalline side chain polyethers on a methacrylic backbone could be built and it was thought to be interesting to study the phase behaviour of such new structures.

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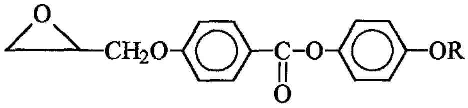
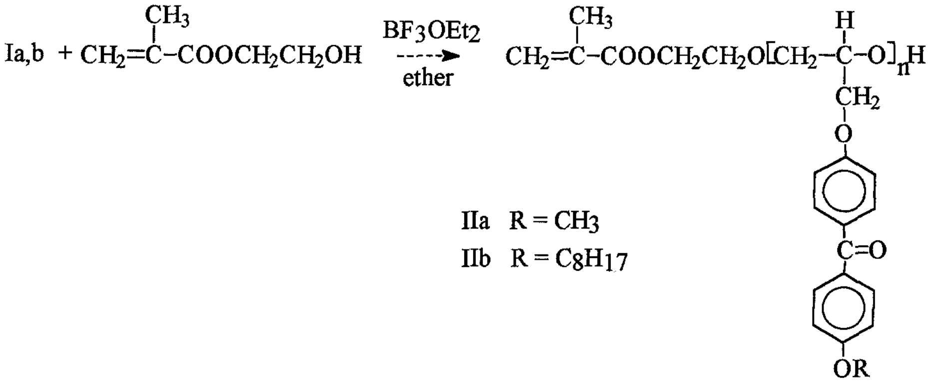


Ia R = CH3, Ib R = C8H17



IIa R = CH3
IIb R = C8H17

RESULTS AND DISCUSSION

The structure of the polyether chain could, in principle, be irregular arising from the different modes of ring-opening of the epoxy monomers, as was found in the case of propylene oxide (KUBISA and PENCZEK 1990). Head to tail polymerization would lead to secondary OH groups at the chain end as depicted in the scheme above.

The ratio [secondary OH]:[primary OH] was determined by ^{1}H-NMR analysis after reaction of the OH end groups with trichloroacetyl isocyanate (TAIC) on macromonomers IIb. The $CHOCONHCOCCl_3$ proton appears as a quintet (four neighbouring protons) at 5,40 ppm. The intensity is approximately equal to one olefinic proton of the methacryl group (5.54 ppm) at the other chain end. No primary hydroxyl could be detected by this method, indicating the predominance of head to tail polymerization with these monomers.

Molar masses could be controlled to a certain extent by the ratio of epoxy monomer to HEMA concentration (see table I). Only at the high ratio's discrepancies with the GPC molar mass become apparent. Although the use of polystyrene standards for the molar mass determination of these oligomers carrying large side groups can give inaccurate values, correlation with vapour phase osmometry proved to be quite satisfactory (see table I) with the exception of IIb.2.

TABLE I : Characterization and Phase Behavior of Macromonomers and their Polymers.

Code	$\frac{[\text{epoxide}]}{[\text{HEMA}]}$	M_n(GPC)	M_n(VPO)	M_n(theor.)*)	$\frac{Mw}{Mn}$(GPC)	Phase transitions
Macromonomers from Ia and HEMA :						
IIa.1	3,3	1240	--	1128	1,14	N 80°I
IIa.2	5,0	1500	1300	1628	1,17	N 89°I
IIa.3	10,0	1790	2620	3537	1,27	N 110°I
Macromonomers from Ib and HEMA :						
IIb.1	2,3	1168	900	1041	1,26	S_A 80°I
IIb.2	5,6	2300	1300	2355	1,20	S_C 44°S_A122°I
IIb.3	10,0	2839	--	4110	1,25	S_A 145°I
Oligomers from macromonomers IIa						
PIIa.1	3,3	2070	--		1,57	N 86°I
pIIa.2	5,0	2600	2600		2,03	N 95°I
pIIa.3	10,0	2900	--		1,96	N 115°I
Polymers from macromonomers IIb						
PIIb1	2,3	3190	2400		2,43	S_A 130°I
PIIb2	5,6	5310	4890		3,20	S_A 170°I
PIIb3	10,0	18406	--		2,58	S_A 174°I
P'IIb1	2,3	10600-49640**)			4,51-1,13	N 172°I
P'IIb2	5,6	5500-38000**)			5,13-1,14	N 167°I

*)From the ratio $\frac{[\text{epoxide}]}{[\text{HEMA}]}$

**)bimodal distribution

Also, molar masses determined from methacrylic and OH head and tail groups (the latter after reaction with TAIC) correlate quite well with the VPO determination, confirming the expected macromonomer structure.

In all macromonomers HEMA incorporation, as required by the activated monomer mechanism, was 100% except for IIb2 (87%) and IIb3 (84%)* .

Attempts to homopolymerize macromonomers IIa and IIb were made using AIBN or ditert.butylperoxide as initiators in solution. Only low molar masses corresponding to coupling of approximately two macromonomers were obtained, presumably due to the low concentration of the double bond and limited solubility of the oligomers. This is in agreement with literature reports on other macromonomer polymerizations (ASAMI and TAKAKI 1985, MASSON et al. 1982, VLEGELS 1987).

Higher molar masses, with in some cases bimodal distributions, presumably due to the inhomogeneity of the medium, were obtained by first polymerizing in solution and then for a second period in bulk (P'IIb1 and P'IIb2). The results are summarised in table I.

Phase behavior

We have studied the phase behavior of the macromonomers IIa and IIb and the corresponding polymers PIIa and PIIb with thermal analysis and polarization microscopy.

From the data in table I the following conclusions could be reached :

Macromonomers IIa showed nematic mesophases. This was also found earlier by Cser for low molar mass (Dp = 5-6) polyethers from Ia (CSER et al. 1985) and by Reesink for hexanediol/BF_3 initiated low molar mass Ia polyethers (REESINK et al. 1996). Clearing temperatures for IIa, however, were much lower: 80°-110°C (IIa1-3) compared to 162°C (CSER, 1985) and 131°C (REESINK, 1996). Since molar masses do not seem much different, this can be due to the methacrylic end group, having a relatively strong influence in these oligomeric products.

The increase in clearing temperatures with increasing molar mass (IIa and also IIb) is a known effect (FINKELMANN and REHAGE 1984, CSER 1985). On changing the methoxysubstituent in IIa to an octoxy-substituent in IIb the nematic phase turns into a smectic phase. This phenomenon is also observed with low molar mass liquid crystals (VAN DER VEEN et al. 1973) and in other side chain liquid crystalline polymers (FINKELMANN 1984).

The oligomers obtained from solution polymerization of IIa and IIb gave also nematic and smectic mesophases arising from the polyether grafts. Especially with PIIb (with slightly higher molar masses than PIIa) the clearing temperatures were higher than those of the parent macromonomers.

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* determined by NMR analysis

The higher molar mass polymers from IIb showed a nematic mesophase instead of the expected smectic one. Apparently the smectic order is no longer possible by steric conditions imparted by the longer backbone. This is remarkable since in other l.c. polymers with the more conventional backbone-spacer-mesogenic group structure higher molar masses resulted in a nematic to smectic phase change (PERCEC et al. 1989, 1992).

EXPERIMENTAL

Synthesis of Ia and Ib :

4-methoxy-phenol was prepared according to Percec's descriptions (RODRIGUEZ and PERCEC 1986) in 50% yield. 4-Octoxy-4-hydroxybiphenyl was prepared from hydroquinone and n-octyl bromide (KLARMANN et al. 1932). Yield of pure 4-octyloxyphenol: 20%.

Both phenols were converted to their 4-hydroxybenzoic esters (VAN METER and KLAUDERMANN 1973). The yields were 49% (p.methoxyphenol-p'-hydroxybenzoate) and 54% (p.octoxyphenol-p'-hydroxybenzoate).

Reactions of these products to Ia and IIb were performed according to literature (CSER et al. 1985). Yield of pure Ia (crystallised from methanol) 55%, yield of pure Ib (crystallised from methanol) 68%. Both products were fully characterised by H^1 NMR.

Polymerizations of Ia and Ib :

All polymerizations were carried out under nitrogen. Initiator (freshly distilled BF_3 etherate), alcohol (HEMA) and solvent (CH_2Cl_2) were placed in a two necked vessel with dropping funnel and stirrer. The monomer solution was added dropwise through a rubber septum by means of a hypodermal syringe during 8 hours at room temperature. After 22 h of total reaction time the polymerization mixture was neutralised with solid CaO (1 h), then the macromonomer was precipitated with cold methanol and dried under vacuum. Typical yield: 50%.

Polymerizations of IIa and IIb :

All polymerizations were carried out under nitrogen. Macromonomer and solvent (toluene or tetrahydrofuran) were placed in a two necked vessel equipped with magnetic stirrer and condenser. The initiator AIBN dissolved in the same solvent (1.5-2.0% by weight) was added through a rubber septum by means of a hypodermic syringe. After 15-20 h at 60°C the polymer was precipitated in cold methanol and dried under vacuum.

To achieve higher molar masses a combined solution-bulk polymerization was carried out: first for 6 h in THF solution, then the solvent was removed so far that a viscous solution was obtained, di-tert.butyl peroxide was added and polymerization was continued for another 6 h at 70°C. Finally, after removal of the rest of the solvent, polymerization was continued for two hours in bulk at 70°C.

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