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Liquid crystalline epoxy resin cured by mesogenic hardening compounds

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Summary

A new type of liquid crystalline epoxy resin functionalized with mesogenic hardening agent was obtained by reacting stoichiometrically 4,4'–bis (2,3–epoxypropoxy) –3,3'5,5'–tetramethyl biphenyl (EPTB) (diepoxide monomer) with 4,4'–bis (ω–carboxy decanoxy) azoxybenzene (CDA10) (mesogenic hardening monomer) at 145°C for 10 min, using tri–n–butylamine as a catalyst. Mesomorphic phase transition behavior for EPTB–CDA10 prepolymer obtained was studied as function of curing time at 140°C by use of DSC and polarized microscopy. When the curing time is shorter than a gelling time (60 min), EPTB–CDA10 showed a liquid crystalline state reminiscent of smectic phase, while that reminiscent of nematic phase, when the curing time is longer than the gelling time. This work indicates that the new type of epoxy resin cured by mesogenic hardening compound can have a liquid crystal state.

Introduction

To date, intense attention has been paid to liquid crystalline thermosetting resins (LCT) such as liquid crystalline (LC) diacrylate polymers (1–3) and epoxy resins (4–10), because LCT's could have characteristic properties originating in their mesogenic repeating unit and so could be used as matrixes for high performance composites, electronic packaging and so on. In paticular, new types of LC epoxy resins have been desired to improve mechanical properties of epoxy resins. Various mesogenic diepoxide monomers were synthesized so far and were reacted with commercial hardening agents such as organic amines. Some of these epoxy resins have been found to show a liquid crystalline state, and their mesomorphic and physical properties were investigated from degree of curing, chemical structure and

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phase transition of mesogenic diepoxide, hardening agent and structure of network. In the past work(4-10), mesogenic diepoxide monomers have been used as a key material to obtain LC epoxy resins, but mesogenic hardening agents have not been used to our knowledge. We beleive that the mesogenic hardening agents give a new way to develop useful LC epoxy resins.

This report communicates to synthesize a new type of LC epoxy resin functionalized with hardening compound, 4,4'-bis (2,3-epoxypropoxy) -3,3',5,5'-tetramethyl biphenyl (EPTB) (diepoxide monomer) - 4,4'-bis (ω-carboxy decanoxy) azoxybenzene (CDA10) (mesogenic hardening agent) epoxy resin (EPTB-CAD10) (see Fig.1).

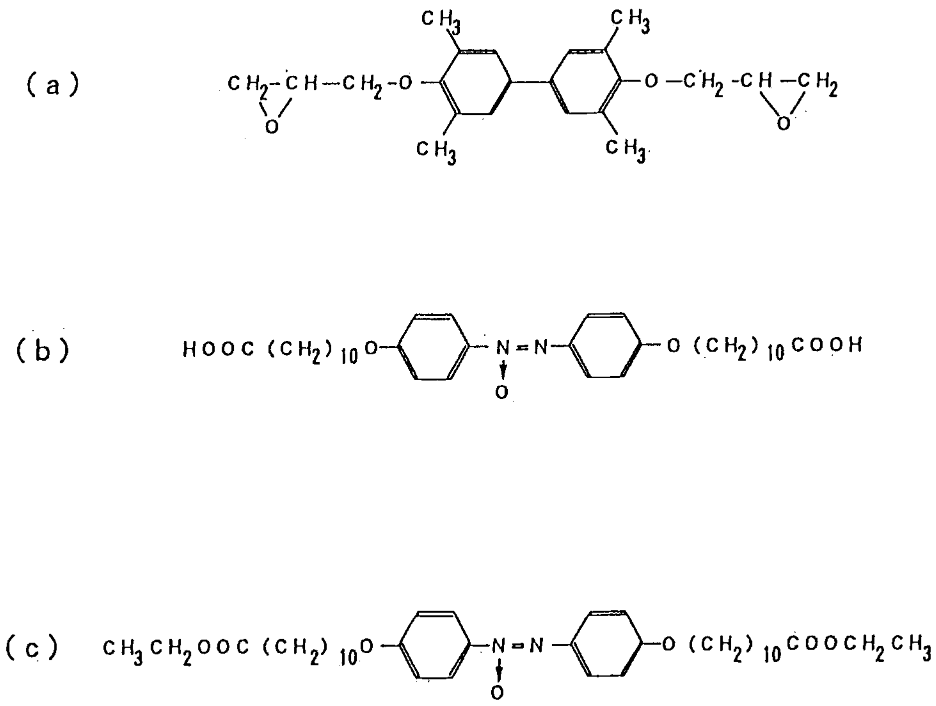

Figure 1. Chemical structures of monomers.

(a). 4,4'-bis (2,3-epoxypropoxy)-3,3',5,5'- tetramethyl biphenyl (EPTB)

(b). 4,4'-bis (ω-carboxydecanoxy) azoxybenzene (CDA10)

(c). 4,4'-bis (ω-ethoxycarbnyl decanoxy) azoxybenzene (EDA10)

Experimental

4,4'-bis (ω-ethoxycarboxy decanoxy) azoxybenzene (EDA10 in Fig.1) was prepared by the following synthetic route; a ethanol solution (200ml) of 4,4'-dihydroxyazoxybenzene (13.42g, 58.3mmol) and t-butoxy potassium (19.63g, 175mmol) was added dropwisely to ethyl 11-bromoundecanoate (119.65g, 408mmol) / ethanol (80ml) solution, refluxing for 24 hrs. The crude crystals precipitated at room temperature were recrystallized from ethanol after washing by water, giving yellow needle crystals (yield : 69%). CDA10 was obtained by hydrolyzing EDA10 compound according to a conventional procedure; EDA10 (26.29g, 40.2mmol) and NaOH (15.78g,281mmol) in 75% ethanol (800ml) were refluxed for 12hrs and the crude crystals obtained were recrystallized from 90% acetic acid solution, giving yellow needle crystals (yield : 87.5%). The CDA10 crystals obtained were judged to be thoroughly pure from NMR, IR, elementary analysis. EPTB was YX4000 of Showa-Shell Co. where the equivalent value of epoxide is 195 equiv./g .

EPTB, CDA10 and tri-n-butylamine (TBA) as a catalyst were mixed in a Teflon beaker and were stirred at about 145°C for 10 min. to obtain epoxy resins of EPTB and CDA10, whose equivalent ratio of CDA10 to EPTB is 1/1 and TBA used was about 3 mol% to CDA10. The EPTB-CDA10 polymers obtained above were used as prepolymer in the subsequent experiments.

Thermal properties were measured by use of a differential scanning calorimeter (DSC) (Seiko-Denshi Co., SSC-5000) at a heating / cooling rate of 5°C/min for EDA10 and CDA10, and 10°C/min for EPTB-CDA polymers. The texture of liquid crystalline phase was determined by an optical microscopy (Nikon, Optiphoto-Pol, XTP-11) equipped with a Mettler FP82 hot stage at a heating / cooling rate of 5° C/min.

Results and discussion

CDA10 had no mesophase and its melting point was 151.9°C, while EDA10 showed a smectic C phase between 64.9 and 88°C. Therefore, it is noted that CDA10 can be a mesogenic monomer.

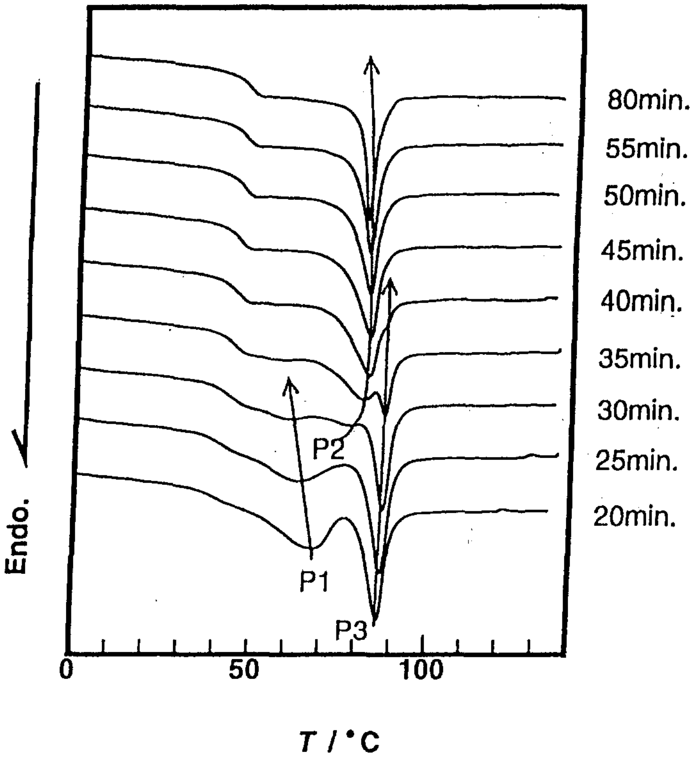

Figure 2. The heating DSC curves for EPTB-CDA10 polymer.
Time (min) in figure is total holding time (t_h) for the prepolymer at 140°C in a DSC pan.

Figure 2 shows DSC curves of EPTB-CDA10 in the heating process, where time (min) in figure is the total holding time (t_h) at 140°C for the prepolymer in a DSC pan; for example, the t_h=25min curve is the 2-nd heating run for the polymer cured at 140°C for 5 min in the 1-st heating run (t_h=20min). The t_h=20min curve shows two peaks near 67°C (P1) and 87°C (P3) respectively, but as the t_h increases, the P1 peak shifts to lower temperatures and decreases in the intensity, and the P3 peak decreases in the intensity, while a new P2 peak and a Tg appear near 80 and 45°C, respectively, when t_h >35 min.. Figure 3 shows photos of liquid crystalline texture at 70°C. The photos show a sand texture, which may be a schlieren texture reminiscent of a smectic state, when t_h=20 min, but a schlieren texture reminiscent of nematic state, when t_h=50 min. From IR spectral studies of curing procedure (11), very recently, we found that a gelling point was about 60 min, when the EPTB-CDA10 prepolymer was cured at 140-150°C and the maximum reaction conversion was 82-87 %. Moreover we estimated the degree of branching (degree of crosslinking) for the fully gelling polymer to be about 5%. Therefore, the changes of

DSC curves and texture of mesophase with t_h are considered to be closely connected with the gelation. When t_h is short, the reaction may proceed to mostly make the polymer chains more elongated, but when t_h is longer, may begin to crosslink and cause a gelation, resulting in gelling around 60 min.. In the gelling state, the crosslinking chains would rather perturb a smectic-like arrangements of mesogenic segments and would prefer to cause a nematic-like arrangements. The X-ray difraction studies are progressing in our laboratories to determine' phase transition and type of mesophase. The results obtained will be in detail reported in the near future but the preliminary data supported the assignments described above.

In conclusion, the present paper briefly reports to develop a new type of LC epoxy resin cured by mesogenic hardening compound, EPTB-CDA10 polymer.

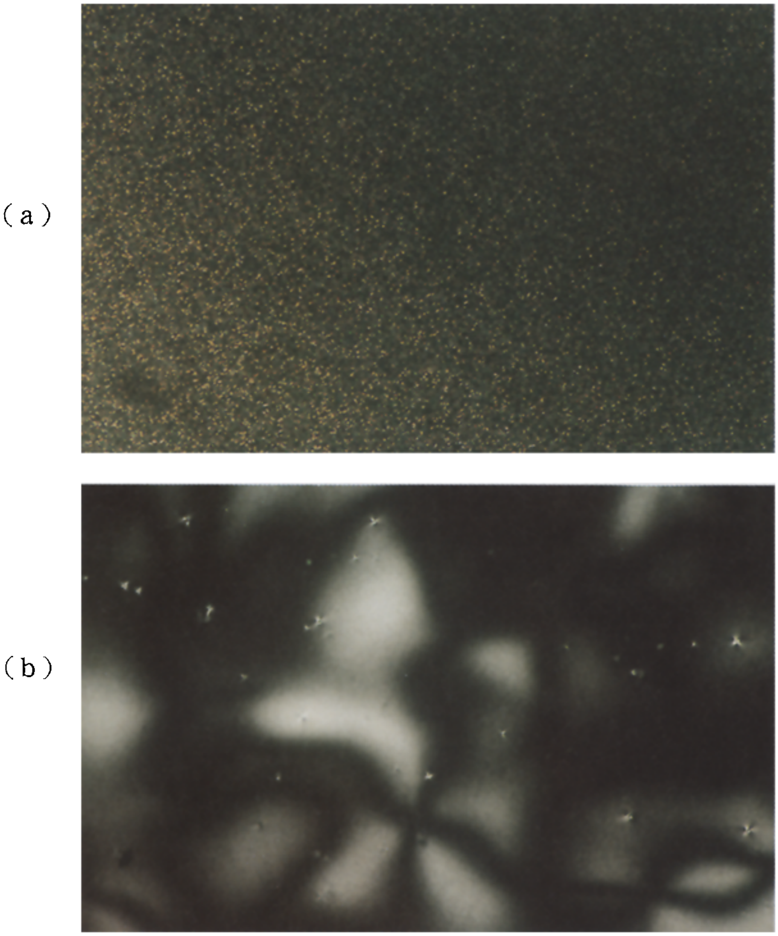

Figure 3. Liquid crystal textures of EPTB-CDA10 observed by Polarized Microscope at 70 °C. (Magnification : ×100)
(a). The total holding time t_h = 20 min. (b). t_h = 50 min.

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