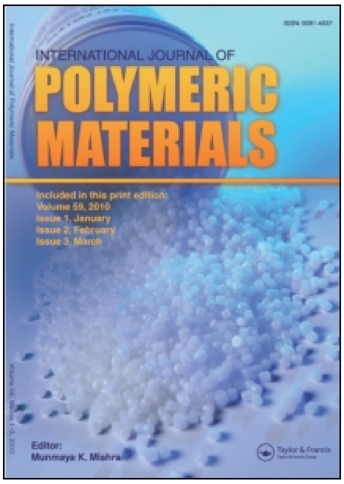


**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Liquid Crystalline Polymers

Naoyuki Koide[a]
[a] Department of Chemistry, Science University of Tokyo, Tokyo, Japan

**To cite this Article** Koide, Naoyuki(1991) 'Liquid Crystalline Polymers', International Journal of Polymeric Materials, 15: 3, 243 — 248

**To link to this Article: DOI:** 10.1080/00914039108041090

**URL:** http://dx.doi.org/10.1080/00914039108041090

*Intern. J. Polymeric Mater.*, 1991, Vol. 15, pp. 243–248
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

# LIQUID CRYSTALLINE POLYMERS

NAOYUKI KOIDE

Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan.

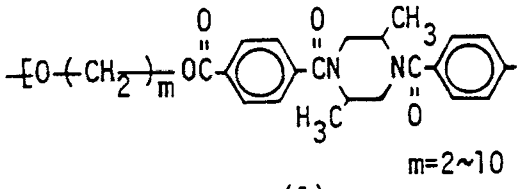
In this article emphasis will be placed on selectively from 45 papers presented at the spring meeting and 33 papers also presented at the fall meeting.

## High Performance Liquid Crystalline Polymers

Many thermotropic liquid crystalline (LC) polyesters have been synthesized and characterized and we expected to have a high degree of molecular orientation and superior mechanical strength. Processed LC polyester materials have superior mechanical strength in the machine direction (MD) but lower mechanical strength in the transverse direction (TD). To solve this problem of mechanical anisotropy, many thermotropic copolyesters are processed with some kinds of filler such as mineral or glass fibers. Another approach used to advance our understanding of the mechanical and the thermal weakness of these materials was presented at the meetings; and involved discussion of (a) copolyesters containing aromatic kink monomer, (b) copolyesters containing amide linkages which have high intermolecular interaction are proposed, (c) synthesis of cholesteric copolyesters which could be taken an accumulated layer of nematic orientation.

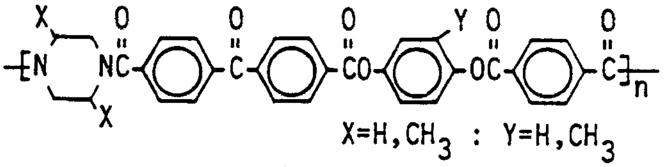
In order to demonstrate the relationship between chemical structures and mechanical properties, various kinds of polyacrylates were synthesized (2996, E608). They suggested that fibrils parallel to the flow direction were needed to obtain a higher value of the modulus. To decrease the mechanical anisotropy, they introduced some substituted aromatic monomers into the copolyarylates, and obtained the higher value of the modulus, and less fibrils and low anisotropy LCP.

N. Agata, *et al.* (1538, E97) synthesized thermotropic liquid crystalline polyesteramides containing piperazine rings. They demonstrated the thermotropic LC properties of semi-rigid polyester amide(1) and rigid



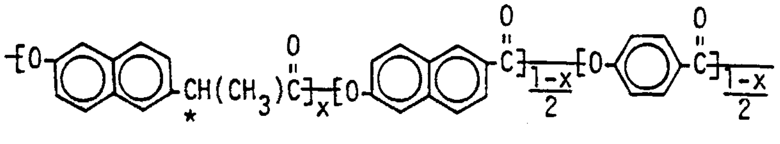
(1)

polyesteramids (2). $T_g$, $T_m$ and $T_i$ (isotropization temperature) of series (1) tended to decrease with the increase of the value of n for the alkyl chains, whereas the enthalpies and entropies change at the $T_m$ showed regular odd-even effects against n for the alkyl chains. Rigid polyesteramide (2) showed Schlieren textures characteristic of nematic liquid crystals. The transition temperatures series(1) were about 100°C lower than these of the homopolyesters.



(2)

N. Koide *et al.*, (2960, E596) has synthesized some cholesteric LC polyesters. They used (s)-2-(6-methoxy-2-naphthyl)propionic acid as a chiral compound. The mesomorphic properties of the three component systems (3) were obtained



(3)

at a concentration of the chiral component ranging from 10% to 50%. A typical finger-printed texture was observed for the copolyesters at 20% content of the chiral component. The cholesteric pitch increased with increasing temperature. All copolyesters of this series were able to be spun from the molten state. The strongest fiber for these copolyesters was obtained from the cholesteric phase. They concluded that the cholesteric orientation would be a significant property in enhancing the mechanical strength.

High performance polymers were obtained by a different polymer processing technique (2990, E606). The thermotropic polyazomethines were synthesized and processed into fibers, sheets or rods by three kinds of processing techniques; melt drawing, injection molding and magnetic orientation. The fibers prepared by melt drawing showed high modulus values (over 100 GPa) however, the modulus decreased with increase in the diameter of the fibers. The injection molded sheets with thickness of 1.0mm exhibited a flexural modulus of about 20GPa. The dynamic flexural modulus of the polymers increased with increasing time in a magnetic field of 10 tesla at 300°C for rods with 2mm diameter.

Fiber orientation and mechanical properties of the injection molded carbon-fiber reinforced LCP(Vectra A215) were investigated by F. Baba *et al.*, (3021, E617). The specimens of A215 were composed of seven layers; two skin layers, secondly two mid layers, a core layer and two transition layers between the mid and the core. The skin and the transition layers contain fibers with a fairly random orientation, whereas the mid layers contain fibers highly oriented to the flow direction, and the core layer contains fibers mainly aligned transverse to the flow direction. Storage modulus of the MD of the core layer were lower than those of TD. They concluded that these results can be explained well by the fiber and the matrix orientation aligned transversely to the flow direction.

Molecular weight distribution measurements of rigid LCP(Vectra type and Zydar type) were carried out by A. Kinugawa *et al.*, (858, E267) using a GPC system. The optimum experimental variables estimated from the data were 60°C for the column temperature, 0.04% for the concentration of the sample, 0.2ml for the injection volume, and 0.3ml a minute for the flow rate. Under these conditions, the reproducible of the chromatograms of LCPs were good, they concluded that the method developed can reveal unrecognized features of the molecular weight distributions of LCPs.

Another approach to interpret the molecular structure of copolyesteramides containing a flexible spacer was presented by T. Uryu *et al.* (3751, E871) using solid-state CP/MAS $^{13}$C NMR. In the solid-state spectrum, alkylene carbon in dialkoxy portions appeared as sharp peaks at 27–70ppm, and the C neighbouring the oxygen appeared at 68.5ppm. Aromatic carbons arose at 110–170ppm. Ester and amide carbon absorptions were separately observed at 168.7 and 171.3ppm in the solution spectrum, which overlapped at 170ppm in the solid-state spectrum.

## Functional Liquid Crystalline Polymers

Side chain type LCPs have been synthesized as the target for functional materials, because molecular motion of mesogenic group and polymer backbone would be decoupled by alkyl spacer, and consequently mesogenic group plays similar behaviour to that observed in low molecular LC.

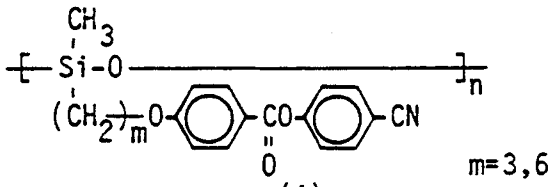
Photosensitive thermotropic LCPs were synthesized and their phase transitions induced by photoirradiation and these materials were studied by two groups. Photochemically induced isothermal phase transitions in LCP were demonstrated by S. Horiuchi *et al.* (2902, E577). They used polyacrylates with mesogenic side chain doped with 5 mol% of 4-butyl-4′-methoxyazobenzene (BMAB), poly(4′-methoxyphenyl-4-acryloxy alkoxybenzoate) [PAPBn], in which the alkyl spacer length $(CH_2)_n$ was varied with n = 2,3,5 and 6, and their copolymers with 4′-methoxy-4-acryloxyalkoxyazobenzene(AAZOm) with m = 3,6 and 11 [Poly-(APBn-co-AAZOm)]. Photoirradiation of PAPB3/BMAB film with 366 nm light caused trans-cis isomerization of BMAB, which induced simultaneously the nematic -isotropic phase transition of the LCP film. This process was reversible and photoirradiation with a 525 nm light which induced cis-trans isomerization restored the system to the initial phase. The phase transition rate decreased with increasing molecular weight and spacer length. On the other hand, the efficiency of the photochemically induced phase transition was found to be the highest in the copolymer with n/m = 3/3.

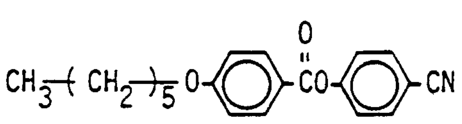
Photosensitive thermotropic LCP for photorecording was reported by Y. Onogi *et al.* (666, 2905, E578). They used a small amount of a guest molecule in the copolymer; because of the inhibitation of the formation of the LC after irradiation of the copolymer. They used the copolymer of ethylene and vinyl alcohol, (Eval) and polysiloxane as a polymer backbone, and azobenzene (Azo) as a photoisomerization molecule. The mixed polymer systems of Eval-azo and APAPA was liquid crystalline at concentrations of less than 7 mol% of azobenzene group. The LCP system containing azobenzene with less than 2 mol% was liquid crystalline even after 1.5h irradiation with 365nm light. Polysiloxanes which containing azobenzene at a concentration of 10 mol% were liquid crystalline at room temperature. When a film of this polymer was irradiated with 365nm light under a masking plate, the fine image was clearly photorecorded by isomerization of the azobenzene group. The recorded image was stable for more than a week, even if the polymer exhibited the LC properties at room temperature.

Photocrosslinking of LCP was studied by C.H. Lee *et al.* (3757, E873) using the LCP having p-phenylene diacrylic acid(PDA) in the main chain. Polyesters having the PDA moieties as mesogenic groups and oligoethylene glycol as flexible spacers exhibited nematic phase. After irradiation with 313nm light transformation to the nematic state, was induced the irradiated parts did not dissolve in chloroform. The formation of cyclobutane rings in the irradiated parts was indicated by IR spectra and $^{13}$CCP/MAS NMR of decreasing double bond. Comparing the efficiency of the photoreaction leading to the formation of interchain crosslinking, the LC phase was found to be significantly higher than the $T_g$ or $T_m$.

M. Ando *et al.* (3769, E877) reported the synthesis of polymer materials using low energy electron beam (EB), 4,4′-bis(acryloyloxyalkyloxy)biphenyl monomers were used as EB-cured materials. The monomers having below 6 methylene bonds showed smectic phase, and the monomers having the odd number of methylene groups showed a more stable liquid crystalline phase than those with an even number. When these monomers were exposed to 30 Mrad, the crosslinking reaction was completed, as demonstrated by DSC and X-ray measurements on an EB-cured polymer.

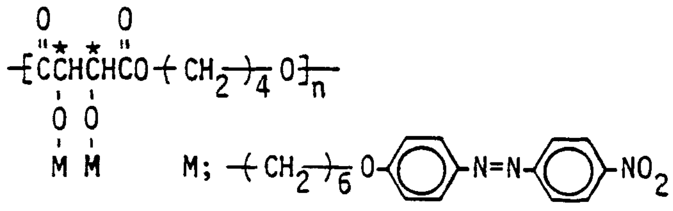
The states of aggregation and the electric field response of the composite systems of LCP/low molecular weight LC were studied by S. Moritomi *et al.* (2453, E423). The mesomorphic state of LCPs was more viscous than the low molecular weight LCs(LMWLC), therefore the magnitude of the response time for the LCP was much greater than that of LMWLC due to the very high viscosity in the mesomorphic state of LCP. They used PCPPS or PCPHS as LCP(4), and CPHOB(5) was used as LMWLC. Application of an a.c. electric field (1KHz) to the composite with a homogeneous alignment caused a decrease in the transmission of light intensity under crossed polarizers due to the occurrence of the homeotropic alignment of the liquid crystalline molecules. The response speed to an a.c. electric field of the LCP increased remarkably on mixing with LMWLC. Application of a low frequency of a.c. electric field to the LCP induced a turbulent flow caused by an ionic current. On the other hand, under a high frequency a.c. electric field, a non-scattering state caused from a homeotropic alignment was formed. A high contrast electro-optic effect was produced by applying these reversible bistable phenomena and these high or nonlight scattering states were stored in the smectic phase with a rise time of the order of msec.


(4)


(5)

Piezoelectric properties of LCP were reported by K. Sato *et al.* (1091, E384). They tried to align and to pole the LCP by the simultaneous application of pulsating current (P.C.) and obtained transparent homeotropically oriented film which had piezoelectric properties, whereas the homeotropically aligned films obtained with an a.c. field did not show any piezoelectricity and a d.c. field caused only turbulence. The piezoelectric voltage obtained from the LCP was much higher than that obtained from conventional piezoelectric polymers, such as PVDF.

Containing a chiral moiety were studied extensively in an attempt to obtain cholestric and ferroelectric LCP's. An optically active polymalate with mesogenic side chain (6) was prepared by S. Abe *et al.* (1075, E376). All polyesters gave both cholesteric and smectic phases. In the smectic phase these polymers were spontaneously aligned in a homeotropic orientation when sandwiched in a glass cell.



(6)

Liquid crystalline side chain type polymers containing an asymmetric carbon atom in the flexible part were reported by T. Kitazume *et al.* (2722, E517). They have already reported the synthesis of the fluorinated ferroelectric liquid crystal with a large spontaneous polarization and quick response time.

The fluorinated ferroelectric liquid crystal polymers were obtained by anionic polymerization. The polymers had a narrow molecular weight distribution and had a molecular weight of around twenty thousand.

Polymer liquid crystals with a nonlinear optical moiety as a mesogenic group were investigated by N. Koide *et al.* (1072, E375). They synthesized 4-methoxy-4′-dialkylamino-αcyanostilbene as the aromatic group with donor and acceptor properties. The methacrylic monomers with 4′-dimethylamino-α-cyanostilbene(DAC) were an enantiotropic liquid crystal exhibiting a thread like optical texture. A powder sample of the polymers gave no second harmonic generation.