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Thermotropic Liquid Crystalline Polymers

8. Optical and Structural Properties of New Nematic and Cholesteric Polymers*

A.M. Mousa, Ya.S. Freidzon, V.P. Shibaev*** and N.A. Platé**

Department of Polymers, Faculty of Chemistry, Moscow State University,
USSR-117234 Moscow, USSR

SUMMARY

A new nematic monomer - p-(ε-acryloyloxycaproyloxy)-p-methoxyphenylbenzoate - was synthesized. A homopolymer of this monomer and its copolymer with cholesteryl-ε-acryloyloxycapronate were prepared by radical polymerization. The homopolymer forms the mesophase of nematic type. The copolymer forms the cholesteric mesophase that shows selective light reflection. The maximum wavelength of the reflected light is equal to 495-500 nm and is not changed on temperature.

INTRODUCTION

In the last few years the synthesis and study of cholesteric thermotropic liquid crystalline (LC) polymers attracted much attention due to the unique optical properties of these polymers /1-4/. The incorporation of chiral monomer units into molecules of the nematic LC polymers to create the cholesteric structure was proposed and realized by us and H.Ringsdorf /3,5/. The present work is a continuation and development of this idea being applied to new nematic and cholesteric LC polymers.

To prepare a nematic polymer the new nematic monomer - p-(ε-acryloyloxycaproyloxy)-p-methoxyphenylbenzoate - (AM-5) was synthesized

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* Part 7. R. V. Talroze, V. V. Sinitzyn, V. P. Shibaev, N. A. Platé Polymer Bull. 6, 309 (1982)

** Present address: Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

*** To whom all correspondence should be addressed

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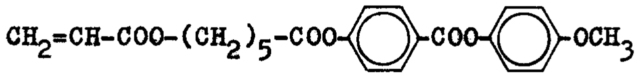
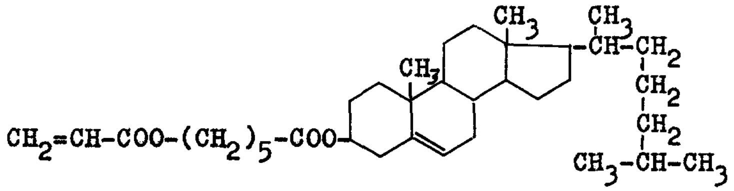


In order to create the cholesteric structure, a copolymer was obtained by copolymerization of the monomer AM-5 with chiral monomer - cholesteryl-ε-acryloyloxycapronate (ChA-5) /6/



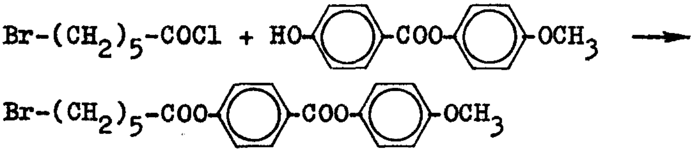
It should be noted that cholesteric polymers being described sofar in the literature are all of the methacrylate type (except polysiloxanes /4/) and are characterized.by elevated glass transition temperatures (T_g) situated in the range of 90-100°C. The choice of acrylate comonomers in this work was made in order to have cholesteric polymer with lower T_g values and wider temperature range of the mesophase state.

EXPERIMENTAL

1. Synthesis of monomers

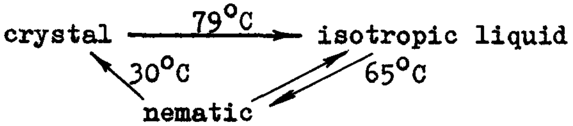
a) p-methoxyphenyl-p-hydroxybenzoate (I) was prepared by condensation of p-methoxyphenol with p-hydroxybenzoic acid according to the procedure /7/.

b) p-(ε-bromocaproyloxy)-p-methoxyphenylbenzoate (II) was synthesised as follows

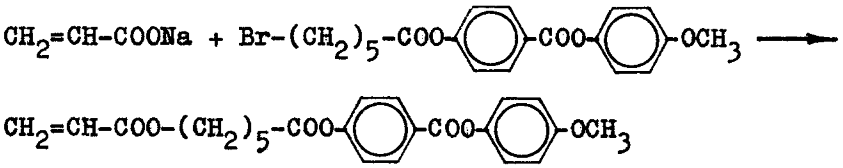


To a solution of 0.03 moles of I in 150 ml of purified THF 0.04 moles of pure triethylamine was added followed by a drop-wise addition of 0.04 moles of

ε-bromocaproylchloride,with stirring for two hours. Then 100 ml of ether was added and solution was washed with water many times and dried with anhydrous $MgSO_4$. After removal of solvent the white crude product was recrystallized twice from ether-methanol mixture. The purity was verified by thin layer chromatography using "Silufol" plates. The pure substance II forms monotropic liquid crystalline phase of nematic type with the transitions temperatures



c) p-(ε -acryloyloxycaproyloxy)-p-methoxyphenylbenzoate was synthesized as follows



3.5 g of substance II were dissolved in 30 ml of hexamethylphosphoramide, then 1.5 g of sodium acrylate were added by stirring and stirring was continued for 6 hours at room temperature. Then 100 ml of ether were added to the mixture and solution was washed with water and dried with anhydrous $MgSO_4$. After removal of solvent the crude product was purified by using column chromatography. Microanalysis and IR-spectroscopy were used to verify the composition and structure of the monomer.

d) cholesteryl-ε-acryloyloxycapronate (ChA-5) was synthesized according to the method described in /6/.

2. Synthesis of polymers

The homopolymer and copolymer were obtained by radical polymerization in benzene and products were precipitated with methanol. The composition of copolymer was determined from UV-spectra.

3. Study of physical properties

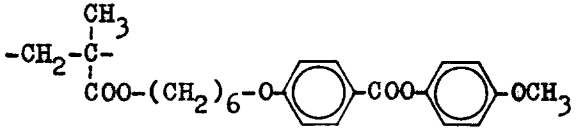
The MIN-8 polarizing microscope with a hot-stage and a photocamera was used to study the optical textures and temperatures of transitions. The selective reflection of the copolymer was recorded by using the spectrophotometer SF-18. The heats of transition were determined by using a differential scanning microcalorimeter DSM-2. X-ray analysis has been performed by using URS-55 with a CuK_α -radiation.

RESULTS AND DISCUSSION

The microscopic study of monomer AM-5 shows that this monomer undergoes the following structural transformations. At 65°C it melts forming an isotropic melt. If this melt is cooled down to 50°C a texture characteristic for low molecular weight liquid crystals of the nematic type appears. Being cooled below this temperatue the monomer starts to crystallize.

The homopolymer PAM-5 shows a birefringence which disappears at 105°C. The observed texture looks like the texture of nematic polymers observed earlier /8/. On X-ray diagram of the PAM-5 only one amorphous halo is observed at wide angles and corresponds to 0.52 nm. No reflections are observed at small angles. Results of X-ray analysis in combination with the observed texture are in favour of the nematic orderliness of the mesophase.

Results of thermal analysis of the PAM-5 shows that on the DSC-curve a shift is observed at 15°C which corresponds to T_g and an exotermal peak at 105°C corresponding to the clearing temperature (T_{cl}). The heat of the latter transition is equal to 2.1 J/g. The polymer with the same mosogenic group but having backbone chain of methacrylate type and another spacer was described in /9/:



This latter polymer forms the nematic mesophase with T_g=95°C; T_{cl}=105°C and ΔH_{cl}=2.1 J/g. One can see that both polymers have the same values of T_{cl} and ΔH_{cl}, but differ significantly in their T_g values. PAM-5 is characterized by essentially lower T_g and hence a larger temperature interval of the mesophase (15°C - 105°C). This can be explained by presence of acrylate main chain instead of methacrylate which leads to the increase of chain flexibility. The fact that neither T_{cl} nor ΔH_{cl} are changed confirms the idea that the character of mesophase is defined in this case only by mesogenic groups

As it has been mentioned before, a number of work has been published concerning the synthesis of cholesteric mesophase by copolymerization of nematic monomers with chiral ones. Copolymers described by us earlier, derivatives of cyanodiphenyl and chiral monomer cholesteryl-$\mathcal{E}$-acryloyloxycapronate (ChA-5) were characterized by selective reflection of visible light. The wavelength of the reflected light is found to be decreased by raizing the temperature /10/. The copolymer of AM-5 and ChA-5 which contains 35 mol.% of cholesteryl units, synthesized in this work has T_g=48°C and T_{cl}=103°C. All over the mesophase the corresponding polymeric film shows selective light reflection which is an indication of the cholesteric type of the structure. The maximum wavelength (λ_{max}) of the reflected light which is equal to 495-500 nm is not changed with temperature which is different from the case described in /10/.

The X-ray diagram of the copolymer shows four reflexes, one amorphous halo with a interplanar distance

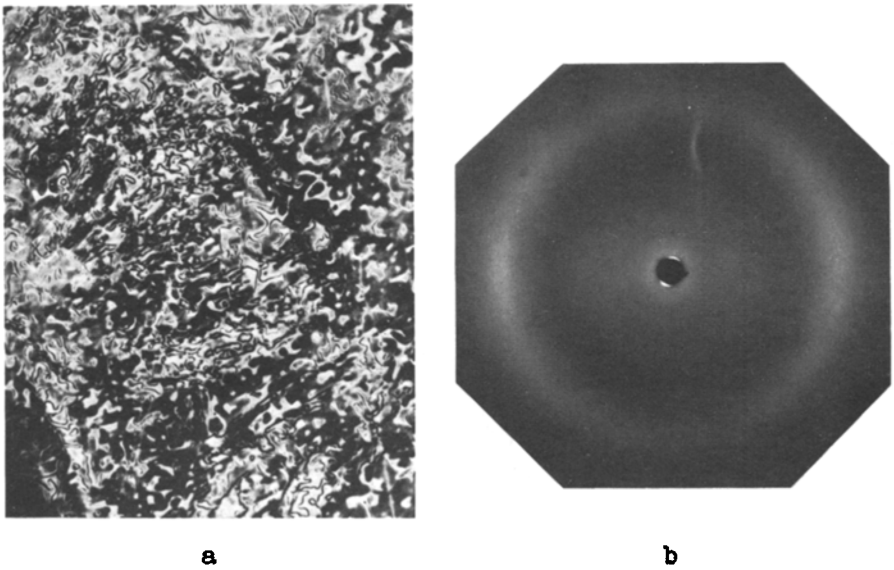


Fig.1. Optical microphotograph (a) and X-ray diagram (b) of nematic texture of polymer PAM-5

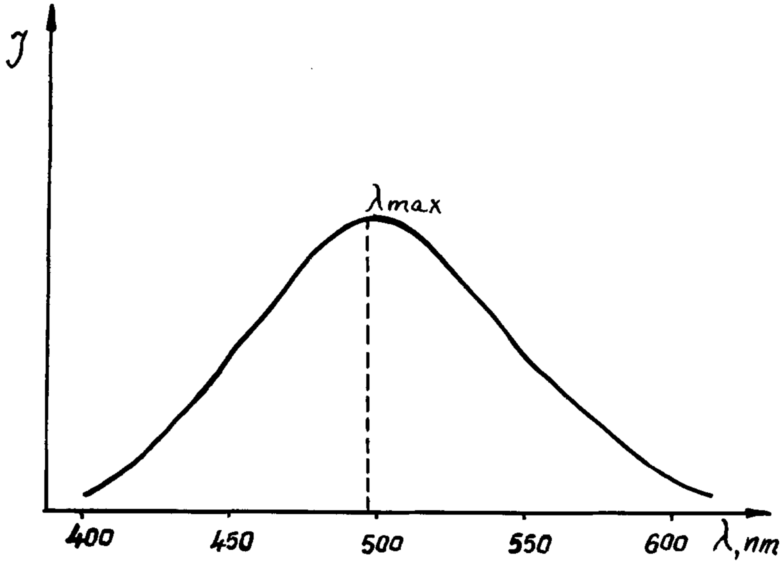


Fig.2. Intensity of reflected light as a function of wavelength for copolymer AM-5/ChA-5

0.54 nm and three small angle reflexes (Table).

TABLE

Interplanar distances of homopolymers PAM-5, PChA-5 and copolymer AM-5 with ChA-5

Polymer	Interplanar distances, nm			
	$d_1 \pm 0.01$	$d_2 \pm 0.02$	$d_3 \pm 0.05$	$d_4 \pm 0.1$
PAM-5	0.52	-	-	-
PChA-5	0.60	1.58	2.40	4.8
Copolymer	0.54	1.57	2.49	4.6

It can be seen from these data that d_1 which corresponds to the distance between neighbouring side groups in the polymeric molecules under consideration, has a value for copolymer being intermediate between the corresponding distances for both homopolymers. Small angle reflexes are practically the same in both copolymer and PChA-5 which can be explained that the type of packing of the cholesteryl groups is almost the same in both polymers. Detailed study of the structure and properties of the synthesized polymers is continued.

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