Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Thermal Changes in Polymers with Liquid Crystalline Order

V. V. Tsukruk [a b] , V. V. Shilov [a b] , V. S. Grebneva [a b] , I. I. Konstantinov [a b] , Y. S. Lipatov [a b] & Y. B. Amerik [b a]

[a] Institute of Macromolecular Chemistry, 252160, Kiev, USSR
[b] Institute of Petrochemical Synthesis, 103073, Moscow, USSR

To cite this article: V. V. Tsukruk , V. V. Shilov , V. S. Grebneva , I. I. Konstantinov , Y. S. Lipatov & Y. B. Amerik (1982): Thermal Changes in Polymers with Liquid Crystalline Order, Molecular Crystals and Liquid Crystals, 82:7, 215-219

To link to this article: http://dx.doi.org/10.1080/01406568208247006

Mol. Cryst. Liq. Cryst. Vol. 82 (Letters), pp. 215-219
0140-6566/82/8207-0215$06.50/0

THERMAL CHANGES IN POLYMERS WITH LIQUID CRYSTALLINE ORDER .

V.V.Tsukruk,V.V.Shilov,V.S.Grebneva,
I.I.Konstantinov,Y.S.Lipatov,Y.B.Amerik

Institute of Macromolecular Chemistry,
252160,Kiev,UkSSR
Institute of Petrochemical Synthesis,
103073,Moscow,USSR

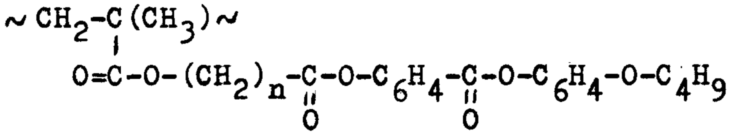
(Submitted for Publication May 4, 1981, Revised May 5, 1982)

Abstract : X-ray study of a number of polymers with mesogenic side groups has been carried out in a wide temperature range.It has been demonstrated that thermal changes in liquid crystalline ordering are determined by the change in main chain mobility.

Structural investigations of polymers with mesogenic side groups point to the existance of LC structures in a glassy state /1/ .LC ordering is supposed to be invariable up to transition into LC state /2/ .This fact gives a good possibility to study the LC polymers at room temperatures,i.e. in the glassy state of polymers.

Recently we have shown that for some polymers with azobenzene side groups the increase of temperature leads to a great and reversible increase in peak intensities on X-ray diffraction curves /3,4/. We explain this effect by the improvement of LC ordering because of the increase of mobility of the main chain.

To elucidate the peculiarities of the thermal changes and the role of the polymer main chain in this process we have investigated some polymers with various length of the spacer-groups. The LC polymers of a general formula have been used :



$$\begin{array}{l} \sim CH_2-\underset{|}{C}(CH_3)\sim \\ \qquad O{=}C-O-(CH_2)_n-\underset{\overset{\|}{O}}{C}-O-C_6H_4-\underset{\overset{\|}{O}}{C}-O-C_6H_4-O-C_4H_9 \end{array}$$

with n=0,3,10 (PM-n) .

X-ray diffraction curves for PM-n were obtained with an automatic diffractometer having a pinhole collimation with CuK_a radiation.

Sharp peaks on low-angle diffraction curves (Fig.1) are indicative of a smectic structure in polymers /1/.

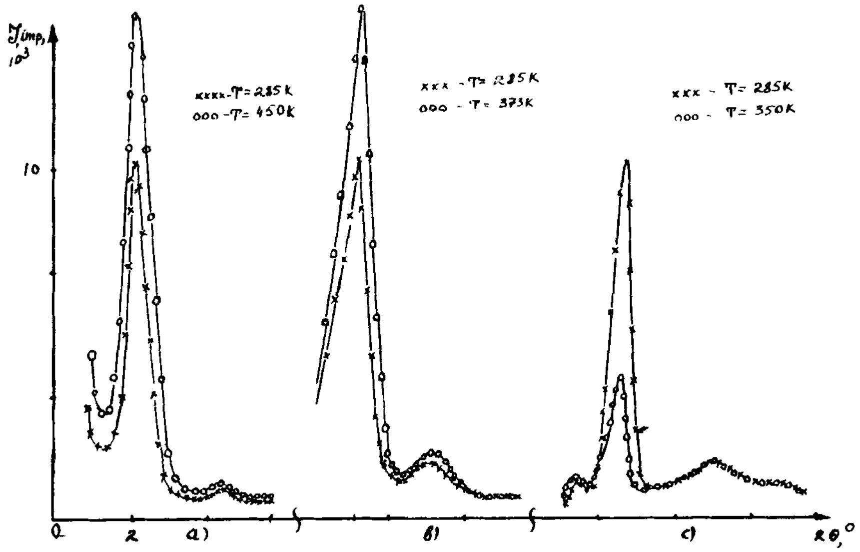


Fig.I.Diffraction curves a)PM-0, b)PM-3,c)PM-IO

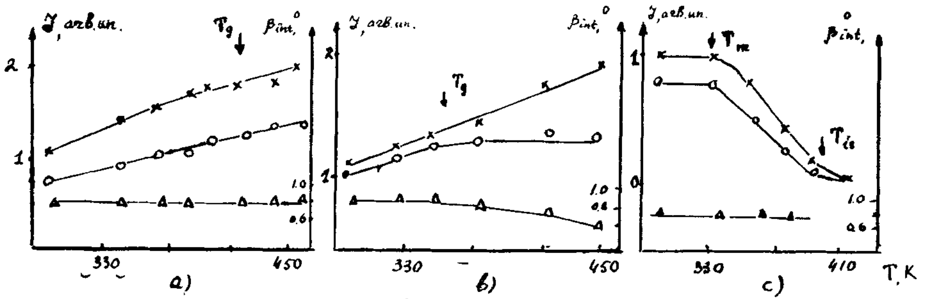


Fig.2.Peak intensity (xxxx-I_{max}),integral intensity (oooo-I_{int}),integral peak width (ΔΔΔΔ - β_{int}) as a function of temperature (transition temperature are marked with arrows). a)PM-0,b)PM-3,c)PM-IO.

The increase in the intensities of low-angle peaks with temperature is similar both for PM-0 and other polymers /3,4/.If our earlier assumption is true,the thermal changes will be dependent on the length of spacer-groups.Moreover the temperature changes in polymers with independent packing of mesogenic groups and main chains will be analogous to the changes in low-molecular LC /5/.

In fact,the temperature variations are changed with lengthening of spacer groups (see Fig.2,PM-3).And,finally,the unusual thermal effect vanish in polymer with independent packing of mesogenic groups and the main chain (PM-10,Fig.2).In the last case the formation of LC order is not affected by the mobility of the main chain.Apparently the improvement of LC ordering in polymers with the increase of temperature is primarily determined by the mobility of the main chain.

According to our calculations the changes in intensities of low-angle peaks should be associated with variations of concentration and sizes of LC domains /6/

It is neccessary to note,that the termal changes in X-ray scattering in LC polymers differ from thouse corresponding to partially crystalline and ladder polymers /7/.As is known the increase of low-angle diffraction peak intensity in partially crystalline polymers is caused by growing of electron density fluctuation resulting from surface melting on crystallities.And the increase of intensity of low-angle peaks in ladder polymers is connected with redistribution of electron density due to the thermal expansion.

Polymers with mesogenic side groups do not follow either of these schemes.In such polymers the increase of temperature leads to the increase both of concentration and sizes of LC domains determined by the changes of mobility of the main chains.

1. S.B.Clough,A.Blumstein,A.de Vries,ACS Polymer Prepr.,18,1,(1977)
2.J.H.Wendorff,H.Finkelmann,H.Ringsdorf. J.Polymer Sci., Polym.Symp., 63,245 (1978)
3.Yu.S.Lipatov et al, in: Adv.Liquid Crystal Res.& Applic.,Ed.L.Bata,Oxford,v.2, 943 (1980)
4.V.V.Tsukruk et al, Acta Polymerica,33,63 (1982)
5.The Molecular Physics of Liquid Crystals,Ed.G.R. Luckhurst,G.W.Gray,Academic Press,314 (1979)
6.Y.S.Lipatov,V.Tsukruk,V.Shilov,Makromol.Chem.(1982)
7.D.Ya.Tsvankin et al,Vysokomol.Soedin.,Ser.A, 21, 2126 (1979)