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Order and Liquid Crystalline Phase Behavior of Polyacid–Tertiary Amine Complexes

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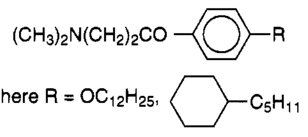
Introduction. Classical liquid crystals are well-known to be designed on the basis of either mesogen-containing organic molecules or molecules having amphiphilic structure. The number of LC compounds is greatly increased in the last few years by means of the noncovalent binding of complementary molecules.[1–5] It permits us to design typical mesogenic molecules, to regulate their shape and length, and to create new low molecular mass and polymer liquid crystals.

The question arises whether this approach is useful for creating amphiphilic structure in polymers that could contribute to thermotropic mesomorphic behavior. Such noncovalent bonded structures can be obtained in different chemical reactions between polyelectrolytes and corresponding low molecular mass reagents. As an example, reactions between polyacids and low molecular mass amines may be considered which should lead to different products by the variation of the reaction medium polarity or by carrying out the reaction at the air–water interface.

The main objective of this paper is to study the relationship between the chemical structure of polyacid–amine complexes in the bulky state and their ability to form ordered mesomorphic phases.

Systems based on linear polyacids like poly(acrylic acid) (PAA) and poly(methacrylic acid (PMAA) and tertiary amines (AC$_n$) of the following structure are



studied. The variation of the amine molecule helps us to understand the influence of its structure (nonmesogenic or mesogenic-like) on the ordering behavior of the polymer system as a whole.

Experimental Section. Materials. β-(Dimethylamino)-4-(dodecyloxy)propiophenone (AC12) and β-(dimethylamino)-4-(pentylcyclohexyl)propiophenone (AC5) were synthesized as described in ref 6. PAA (Aldrich) with M_w = 250 000 (T_g = 106 °C) was used. PMAA was synthesized according to the method described in ref 7 without additional treatment. Samples are prepared by mixing corresponding amounts of 0.1 M acid and amine solutions in ethanol followed by the precipitation of the reaction product. The latter is purified by the additional amount of alcohol.

Methods. A Mettler DSC (TA 4000) was used to investigate the thermal behavior of complexes and initial components with the heating rate equal to 10 K/min.

X-ray measurements were performed using a Rotaflex RU-200 "Rigaku Dmax-RC" instrument (Ni-filtered Cu Kα radiation, transmission mode).

An optical microscope POLAM L-312 equipped with a heating stage RNMK-05 (Boetius) was used for optical texture observations.

Results and Discussion. We have shown in our previous publications[8,9] that polyacids and tertiary amines mentioned build solid hydrogen bond complexes with the strong proton polarization. The characteristic complex composition corresponds to the ratio 2 COOH groups:1 amine and does not depend on the structure of the polyacid (PAA or PMAA).

The 2:1 complexes of polyacids with amines precipitating out of the reaction mixture are solid substances that show very low crystallinities (about 2–3%). This is evidenced in the X-ray diagrams (Figure 1, curve 1) as diffraction maxima of low intensity at wide angles. Low crystallinity means that the H-bonding prevents the crystallization of amine when complexes are formed at the conditions mentioned above. At the same time the small-angle maximum of the high intensity combined with an intensive amorphous halo also exists.

The melting of complexes accompanied by the corresponding endothermic DSC peak at T_m (Figure 2, curves 1 and 2) proceeds within the rigid polymer matrix without any change of its aggregative state. Above the melting point the structure of the complexes is characterized by a small-angle maximum and diffuse halo at wide angles of X-ray scattering (Figure 1, curve 2) and optically anisotropic but noncharacteristic texture. These data indicate the order of the complex structure above the melting point. Interlayer distance d corresponding to the small-angle maximum does not change at T_m (Figure 3, curve 1). It means that below T_m small crystalline regions coexist with the noncrystalline ordered phase whereas above T_m only one ordered structure exists.

Such ordered structure is the characteristic feature of all the complexes studied. It exists in a very broad temperature range and disappears at the clearing point T_c (Figure 2, curve 1). The endothermic peak at 150 °C corresponds to the disappearance of the small-angle maximum (Figure 1, curve 3) while the birefringent texture also disappears. This transition is reversible although the structure is strongly sensitive to the cooling conditions.

At the same time the d spacing increases with the heating of the sample within the temperature range corresponding to the ordered structure of PAA complexes (Figure 2). One can suppose that the change of the slope (Figure 3) in the curve $d(T)$ relates to the complex glass transition, and the small step in the DSC curve (Figure 2, curve 1) in the same temperature range confirms this idea. The T_g of the 2:1 complex (90 °C) is lower than that for pure PAA (106 °C).

Contrary to PAA complexes d spacing in complexes of PMAA does not change practically till the clearing point (Figure 3, curve 3), indicating a much higher glass transition temperature.

The orientation of the complex sample above T_g results in the textured X-ray pattern (Figure 4 (1)). The small-angle maximum (d = 4.7 nm) looks like two arcs at the equator of the X-ray pattern, indicating the normal orientation of amine fragments to the deformation axes. Comparison of d values for 2:1 complexes (4.7 nm for PAA:AC12 and 4.1 nm for PAA:AC5) with the certain length of amine molecules and chain thickness

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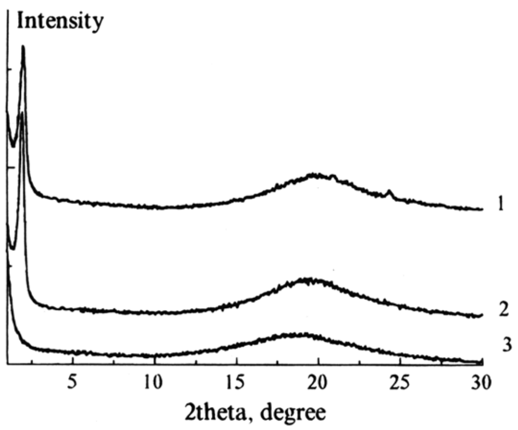

Figure 1. X-ray diffraction patterns of a 2:1 complex of PAA: AC12 at 20 (1), 100 (2), and 150 °C (3).

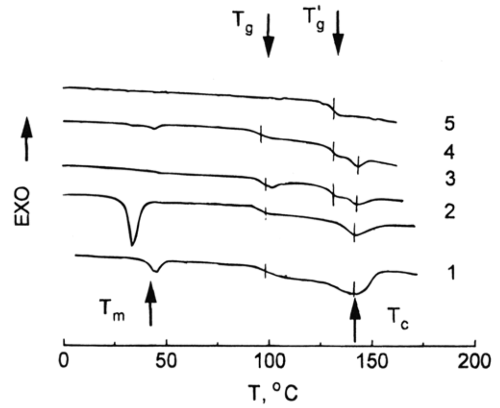

Figure 2. DSC curves for complexes PAA-AC12 2:1 (1, 2) and 5:1 (3, 4) and PAA (5) after solvent evaporation (1, 3). Curves 2, 4, and5: second heating.

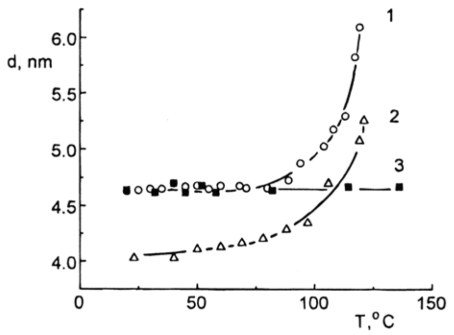

Figure 3. Temperature dependence of interlayer distance d for complexes PAA-AC12 2:1(1) and 5:1 (2) and PMAA-AC12 2:1 (3).

shows the formation of the smectic-like structure with overlapped alkyl groups according to the scheme given in Figure 4 (2).

The change of the complex composition influences the structure of the smectic-like phase: with the decrease of the amine fragment content in the complex the small-angle maximum shifts to the wide-angle region. It corresponds to the 15% decrease of the interlayer distance when the content of amine residues is about 10−20%. It is necessary to point out that this low content of the amine residues is enough to induce the kind of layer order in the polymer H-bond complexes.

The temperature curve for the d spacing in the 5:1 complex (Figure 3, curve 2) is similar to that for the 2:1 complex discussed above (Figure 3, curve 1), indicating practically the same glass transition temperature, although the change of the copolymer composition should contribute to the glass transition temperature.

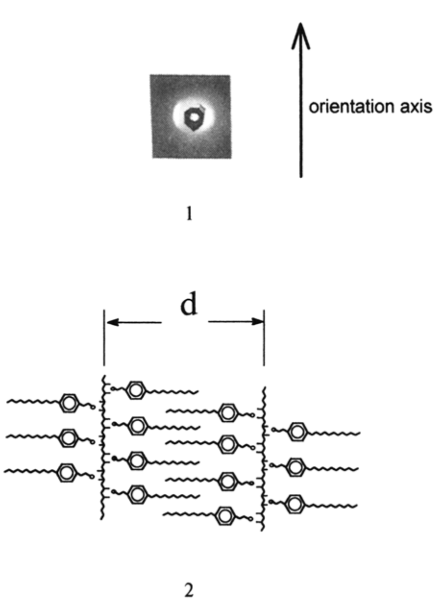

Figure 4. Small-angle X-ray diffraction pattern (1) and model (2) of the PA-ACn (2:1) complex.

To explain such unexpected behavior, one has to discuss the structure of complexes containing small amounts (less than in the characteristic complex) of amine residues ("diluted" complexes). One can suppose the block distribution of different units along the chain that can result in the microphase separation. The analyses of the DSC curves of "diluted" complexes (Figure 2, curves 3 and 4) cooled after the heating above the clearing point shows two different steps that can be attributed to two different T_g. The first T_g correlates with the T_g indicated from X-ray data and coincides with that for the 2:1 complex. The second T'_g corresponds to the T_g of the waterless PAA annealed at 140 °C (Figure 2, curve 5). This makes the idea on the possible microphase separation (PAA and 2:1 complex blocks) in "diluted" polyacid complexes quite reasonable, although we did not observe two different morphological structures by means of the optical microscopy because of the noncharacteristic birefringent texture of the ordered regions.

Coming back to the main reason for the formation of smectic-like supramolecular structure in characteristic complexes studied, one can compare their structure with that of the lamellar phase. The latter results from the packing of amphiphilic molecules of amine hydrochlorides in water.[10] We can suppose that weak amphiphilic properties of amine molecules become stronger due to hydrogen bonding with polyacids. As a result a microheterogeneous system appears. It contains regions where alkyl aromatic residues and polar groups are located. In this case, the polyacid performs like an "aqueous" interlayer. Such complexes could be considered as a particular group of ordered systems which is displaced at the boundary between thermotropic and lyotropic liquid crystals.

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