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New Series of Liquid Crystalline Polyacrylates with Wide Mesomorphic Temperature Range

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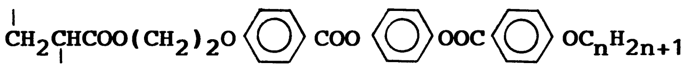
New liquid crystalline polyacrylates having ester linkages were synthesized. The methoxy and ethoxy derivatives among these polyacrylates exhibit a thermally stable nematic phase with a wide temperature range useful for gas-liquid chromatography.

Liquid crystals are anisotropic liquids and they exhibit interesting solvent properties due to the ordered arrangement of their molecules. These unique solvent properties of liquid crystals have been used as the stationary phase in gas-liquid chromatography(GLC)for the separations of many isomers.1,2) Until recently, mainly monomeric rod-like molecules have been utilized as the mesomorphic stationary phases. However, these monomeric liquid crystalline phases suffer from column bleed as a result of volatility and thermal instability at high temperatures. A significant advancement in this respect was achieved by employing mesomorphic side-chain polymers as the stationary phase.3) Recently, these liquid crystalline polymers have been with good success applied in capillary column for the GLC separation of polycyclic aromatic hydrocarbons.4-7)

Unfortunately, it is also known that polymeric liquid crystals synthesized to date have a disadvantage that they exhibit high glass-mesomorphic transition temperatures, which precludes their application to separations of volatile solutes such as xylenes. Therefore, it is of great importance to find new liquid crystalline polymers exhibiting a wide mesomorphic temperature range and a thermal stability. We wish to report in this work a new series of liquid crystalline polyacrylates with the following structure which are thermally stable and exhibit a broadened mesomorphic range.



(n=1-8)

The transition temperatures and the liquid crystalline phases of the polyacrylates as well as the monomers studied here are summarized in Tables 1 and 2. A comparison between Tables 1 and 2 shows that the polymers give low glass-mesomorphic transition and high mesomorphic-isotropic transition temperatures, i.e., broadened mesomorphic temperature range compared with the monomers. In addition, it should be pointed out that in the case of these polyacrylates the length of the end alkoxy chain has much greater effect on the liquid crystalline phase transitions. The smectic phases can be observed in the polymer series for the member with a relatively short alkoxy chain(C_4), and the nematic phase

Table 1. Transition temperatures of the monomers[a)]

n	transition temp/°C		
	S(C)	N	I
1		112	216
2		122	212
3		136	199
4		121	197
5		114	182
6		103	180
7		100	172
8	80[b)]	102	170

a) I:isotropic, N:nematic, S( ):smectic.
b) monotropic.

Table 2. Transition temperatures and molecular weights(M.W.) of the polymers[a)]

transition temp/°C						
S(IV)	S(III)	S(II)	S(I)	N	I	M.W.
				66	295	4600
				63	288	4700
				64	276	5600
68			100	215	270	5200
75	130		152	245	261	4900
77	129	165	205	249	258	5600
81	140	195	232	254	257	6000
80	133	210	240		255	6500

a) The signs of S( ), N,and I are the same as those in Table 1.

disappears when the alkoxy chain is lengthened to C_8.

Furthermore, it is worthwhile to note that the smectic phases observed in the polymers exhibit smectic polymorphism while the monomer shows only the smectic C state. Under polarizing microscopic observation, the smectic I phase exhibits fan-shaped texture or homeotropic alignment when formed on cooling the nematic phase. At the phase transition from the smectic I to the smectic II phase smectic schlieren texture appears on the homeotropic alignment, and the fan-shaped texture changes to broken fan-shaped texture. From these characteristic textures, it seems likely that the smectic I phase is the smectic A, and the smectic II is the smectic C. On further cooling these textures distinctly change to different smectic texture at the phase transitions which can be detected by differential scanning calorimeter(Shimadzu DT-40). However, the exact classification of the smectic III and IV phases remains unclear since these smectic phases exhibit no well-defined typical smectic textures.

From a practical view of point, the methoxy and ethoxy derivatives among the polyacrylates studied are quite interesting because they exhibit a thermally stable nematic phase with a wide temperature range useful for GLC separations. A study of their application to the stationary phase in GLC is in progress.

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