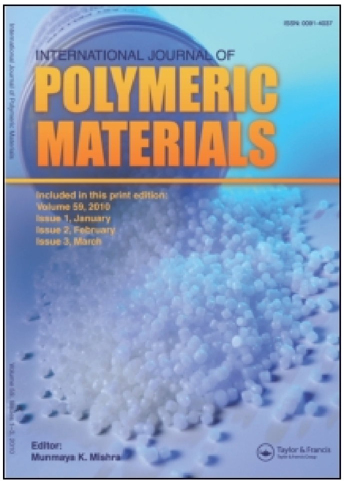

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Investigation of Conformational Behavior and Mobility in Linear Liquid Crystalline Polyesters by ^{13}C Solid State NMR-Spectroscopy

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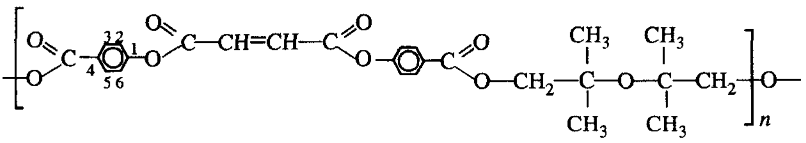
Splitting of resonance signal of CH_2 group of spacer was observed in ^{13}C solid state NMR spectra of liquid crystalline (LC) polyester with siloxane spacer $[-OC-Ph-OOC-CH{=}CH-COO-Ph-COO-CH_2-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-O-]_n$ in LC-state. We consider that there are two conformations of $-COO-CH_2-Si(CH_3)_2$-group of spacer. These conformations are stabilized by steric interactions of CH_2 groups of siloxane fragments with ortho-protons of phenylene rings of mesogene. As a result, there are hindrances to both flips of the phenylene rings and conformational transitions in the spacers.

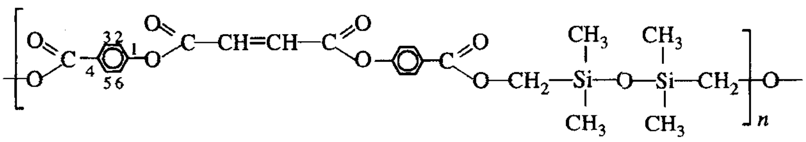
KEY WORDS ^{13}C NMR-spectroscopy, spacer conformation, liquid crystalline polyester, mobility.

INTRODUCTION

The introduction of substituents into the spacer has been traditionally considered to be a factor decreasing the mesophase isotropization temperature.[1] This concept springs from the synthesis of low molecular weight compounds.[2] However, the consideration of the volume and the branching of the aliphatic spacer as the only two factors that determine the mesophase stability at the same mesogene involve certain difficulties. Thus, polymer 1 with a dipropyleneglycol spacer



is not liquid crystalline (LC) (T_g = 35°C, M_n = 10 000), whereas polyester 2 with a siloxane spacer which is even slightly longer



is LC ($T_g = -2°C$, $T_i = 60°C$, $M_n = 6000$). However, they both have five atoms between the mesogenic fragments, and from this viewpoint they are identical.

This fact is in a certain contradiction with general concepts because the volume of the siloxane spacer is incomparably larger than that of the dipropyleneglycol spacer. Naturally, commercial dipropyleneglycol is a mixture of head-to-head, head-to-tail, and tail-to-tail isomers, and also a mixture of stereoisomers. However, it is known to have a insignificant effect on the possibility of mesophase formation and its stability.[3]

EXPERIMENTS AND DISCUSSION

The ^{13}C NMR spectra of polymer 2 recorded in the LC phase, in the isotropic melt (IM) and in solution (S) are presented in Figure 1. NMR spectra were recorded in solution with a Bruker AC 200 spectrometer, and in bulk with a Bruker CXP-100 instrument with Bruker broad band CP/MAS double bearing probe head. To study LC samples we used standard CP pulse sequence with repetition time 2.5 s and contact time 3 ms. In the case of isotropic melt we used one pulse sequence with high power decoupling and relaxation delay 5 s. Speed of sample rotation was about 3–3.5 kHz. It is clear that in the LC melt the signals of carbons in phenylene rings and the spacer are doubled. The doubling of the signals of phenylene rings can be explained relatively simply: the free rotation of these rings is absent in the LC melt, whereas the signal doubling in the spacer induced us to consider spherical molecular models. Although we understand clearly that these models are only tentative, we use them since they make it possible to evaluate steric interactions in the molecule very clearly and relatively correctly. The following result was obtained: in polymer 2 with a bulky siloxane fragment in the spacer, there are two conformations of the $-COO-CH_2-Si(CH_3)_2-$group of the repeat unit. These conformations are stabilized by steric interactions of methyl groups of siloxane fragment with ortho-protons of the phenylene rings of the mesogene. As a result, there are hindrances to both flips of the phenylene rings and conformational transitions in the spacer.

It is evident that LC order increases the energetic barriers between two conformations of $-COO-CH_2-Si(CH_3)_2-$groups of spacer, because these conformational transitions need the destruction of the orientational order of mesogenic units. In some theoretical papers[4] an attempt was made to consider the effect of the external order on the selection of certain conformations in LC state.

Hence, the doubling of signals in the ^{13}C NMR spectrum of polymer 2 in the LC phase is due to two stable conformations of the $-COO-CH_2-Si(CH_3)_2-$ group of macromolecule, which are separated by relatively high conformational barriers induced by the contribution of the external order. This contribution is absent in the isotropic phase. These barriers become lower, and mutual transitions between conformations become free from the viewpoint of NMR. The same phenomenon is observed in solution. The consideration of the molecular model shows that these interactions are absent in polymer 1.

Consequently, it may be concluded that the substituent in the spacer affects the stability of the mesophase of main chain polyesters not only as a result of the purely volume effect but also due to steric interactions. These interactions may lead to the selection of certain conformations that may raise the energetic barriers of conformational transitions increasing thereby the energy necessary for mesophase destruction.

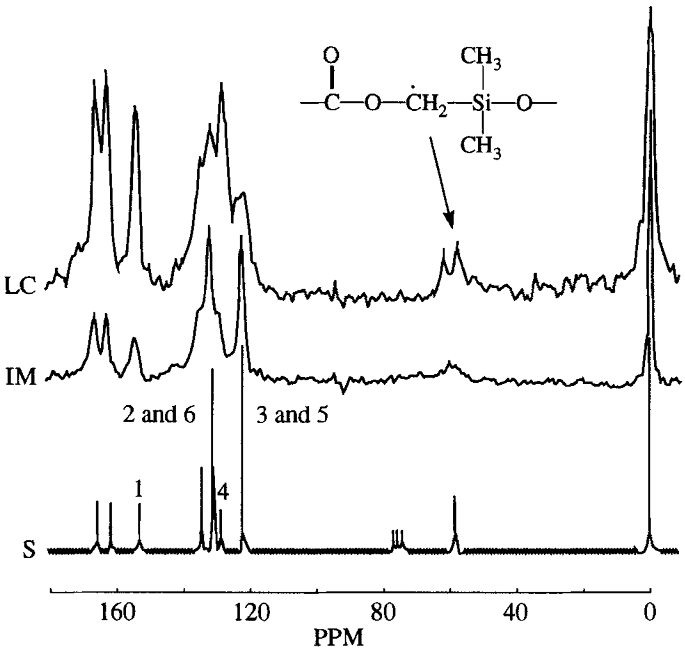


FIGURE 1 ^{13}C NMR spectra of polymer 2 in different phase state: LC, $T = 25°C$; IM, $T = 70°C$; S, $T = 25°C$. The figures near signals correspond to the number of the C-atom in the benzene ring indicated in the chemical formulae.

CONCLUSIONS

This investigation has shown that in spite of the widespread opinion, the existence of methyl substituents does not necessarily decrease isotropization temperature. For example, mesophase thermostability of alkylene-aromatic polyesters is higher than that of their unsubstituted analogs. The existence of steric interactions between alkyl substituents and the mesogene fragment can lead to a considerable stabilization of extended conformations of the macromolecule and to an increase in the energetic barriers of conformational transitions. Therefore, the stability of the LC state can increase.

References

1. Ch. K. Ober, J.-I. Jin, and R. W. Lenz, *Adv. Polym. Sci.*, **59**, 104 (1984).
2. G. W. Gray, *Polymer Liquid Crystals*, Eds. A. Cifferi, W. R. Krigbaum, and R. B. Mayer (Academic Press, New York, 1982), p. 1.
3. E. Chiellini, G. Galli, S. Carrozzino, and B. Gallot, *Macromolecules*, **23**, 2106 (1990).
4. G. R. Luckhurst *Recent Advances in Liquid Crystalline Polymers*, Ed. L. L. Chapoy (Appl. Sci. Publishers, Elsevier, London, 1985), p. 105.