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Thermotropic Behavior of Polyisocyanates

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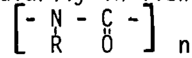
SUMMARY

A polarizing microscope is used to investigate the liquid crystalline phase of polynonylisocyanates. The effect of the degree of polymerization of the chains on the anisotropic-isotropic transition temperature is demonstrated and a discussion within the theory of semi-rigid liquid crystalline polymers is given.

INTRODUCTION

Since their original preparation in 1959 (1,2), poly-isocyanates have been the subject of detailed research, particularily in view of determining the chain rigidity. The chemical structure is  $\left[-\underset{R}{\mathrm{N}}-\underset{\overset{\|}{O}}{\mathrm{C}}-\right]_n$ where R is generally a short aliphatic chain. Complementary studies of intrinsic viscosity (3-15) and light scattering (4,13,14,18) have been performed in various solvents and on variation of the degree of polymerization n. Dielectric relaxation measurements (19-24) have confirmed the existence of aggregation in dilute solution and the nature of the macromolecular structure.

The chain rigidity obtained varies over a large interval of values and depends on the monomer (type and length of side chain R), the experimental method used, and the theoretical model applied in interpretation of the experimental data. Consistently through, the persistence lengths are between 200 and 1000 Å which for a monomer length of around 2 Å is considerable.

In view of the high values of chain rigidity, the appearance of a mesomorphic phase could be expected in these polymers. This was indeed discovered by Aharoni(25-30),in particular in polyisocyanate solutions. Interesting effects(27) were found for the transition temperatures from the crystalline to the nematic and from the nematic to the isotropic phase on variation of the number of carbons present in the side chain R. No studies were made of the variation of the transition temperature with the degree of polymerization. This variation has been examined in other semi-rigid liquid crystalline polymer systems(31-35) and a theoretical discussion has been given (36).

We report here on experimental measurements of the mesomorphic phase transition in thermotropic polynonylisocyanates(PNIC) and compare with the theoretical prediction for the variation with degree of polymerization DP.

THEORY

For a semi-flexible, worm-like chain with strong directional intermolecular forces of quadrupolar symmetry (dispersion, steric), a Landau-de Gennes expansion in the nematic order parameter has been derived(36). The existence of a spontaneously ordered nematic phase can be shown for temperatures

$T < T_c$. The critical temperature T_c for a first order anisotropic-isotropic phase transition, has been given as a function of DP, L, persistence length, q, and intermolecular interaction, v. For $L/q \rightarrow 0$ (rigid rod limit) we find T_c decreases as L decreases with an initial slope which measures the strength of the effective quadrupolar interaction and is independent of chain rigidity. As the chain length increases, the flexible chain limit ($q/L \rightarrow 0$) is approached. Screening of the quadrupolar interaction occurs and limits v until further increase of chain length is no longer effective for ordering of monomer units. The transition temperature T_c then saturates and remains constant as a function of L. The trend to saturation is rapid in flexible chains,for example,using flexible spacers (31). In chains with appreciable values of persistence length, slow flattening of T_c (L) curves at high degrees of polymerization is predicted. The polyisocyanates should be examples of this latter behaviour. The persistence lengths are considerable although tend to decrease at high temperatures (37). The high chain rigidity weakens the effects of the entropic and excluded volume interactions (7), consistent with the assumptions of the model.

The large permanent electric dipoles present along the chain backbone are specific to polyisocyanates and will contribute to the intra-as well as to intermolecular interactions (38). Shielding by the side chains R and the effect on the mesomorphic transition temperature has been discussed previously within the same model (39).

EXPERIMENTAL

The PNIC samples have been kindly donated by Mme Marchal, CRM, Strasbourg (whome we wish to thank for making these studies possible) and were prepared by J. Pierre, Université de Liège (whom we also wish to thank) using the method described in ref. (1,2). Seven fractionated samples, with a polydispersity less than 1.2 and of molecular weights between 16000 and 600000 were studied. The details of the preparation, fractionation and determination of molecular weight have been given in (24).

The phase transition was investigated by polarizing microscope. An example of a characteristic texture in the nematic phase is given in fig.1.

The temperature for the transition from the anisotropic to the isotropic phase is shown in fig.2 and table 1. An increase with increasing DP and a slow saturation at high DP is found in agreement with the theoretical predictions.

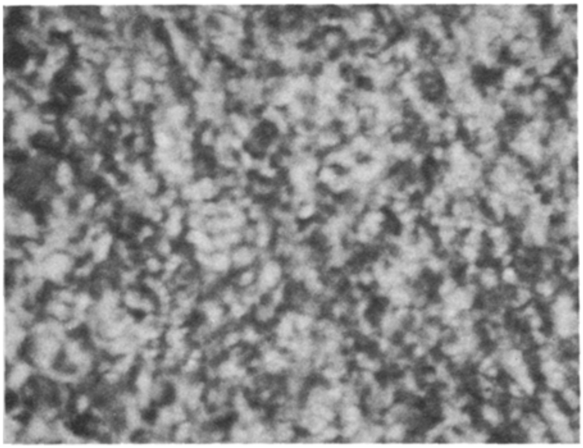


Fig. 1 : Characteristic texture of nematic phase of polynonyl–isocyanate M_w = 16.000

Table 1 : Nematic - Isotropic transition temperature T_c on variation of molecular weight M_w of polynonylcyanates

M_w	16000	25000	66000	104000	160000	360000	600000
T_c (°C)	146	149	159	169	169,3	169	169

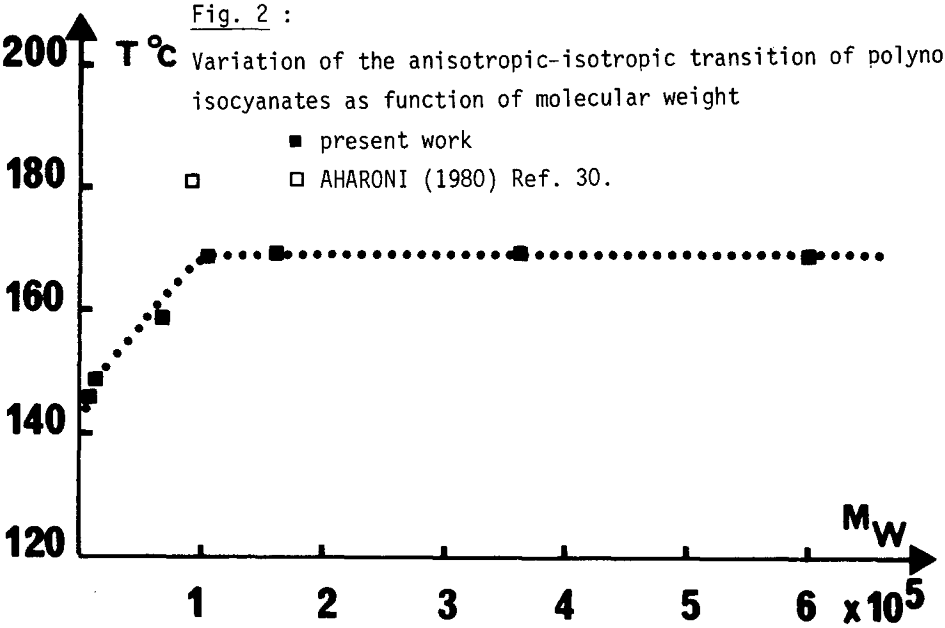


Fig. 2 : Variation of the anisotropic-isotropic transition of polynonylisocyanates as function of molecular weight

CONCLUSIONS

The polyisocyanates are well described by a model of semi-rigid wormlike chains; the results on the nematic-isotropic transition temperature obtained for polynonylisocyanates conform to the predictions of the theory of liquid crystalline polymers within this model. It would be of interest to verify these results for other members of the same family (polybutylisocyanates or polyhexylisocyanates).An evaluation of the persistence length for PNIC is lacking and would be useful as well as further experimental and theoretical studies of phase diagrams in simple solutions (35).

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