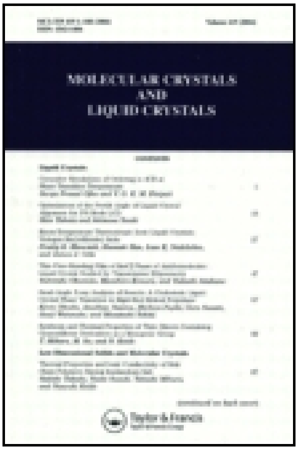

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DYNAMICAL MECHANICAL PROPERTIES OF MAIN CHAIN LIQUID CRYSTALLINE POLYMERS

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Abstract The dynamical mechanical properties as well as the dielectric relaxation properties of liquid crystalline main chain polymers were determined in a temperature range from -150 ^{o} up to 200 ^{o}C both for rigid as well as for semiflexible chain molecules.The presence of a secondary relaxation process well below room temperature and of a primary glass relaxation at temperatures between 65 and 110 ^{o} C was observed for these polymers These processes were found to couple strongly to the dynamical mechanical properties as well as to the dielectrical properties.A surprising finding is the large relaxation strength and the corresponding energy dissipation associated with the low temperature ß-relaxation in these polymers with restricted chain flexibility.

Introduction

The mechanical properties of polymers are known to couple strongly to relaxation processes taking place within the glassy or partially crystalline state as well as within the glass transition region [1,2]. The occurrence of these relaxation processes causes the storage moduli to decrease stepwise with increasing temperature and the loss moduli to display a maximum.

Data on the relaxation properties of semiflexible and rigid thermotropic main chain polymers are , however, sparse [3-5]. The general finding is that these main chain polymer tend to display a partially crystalline state at lower temperatures. So it is predominantly the chain rigidity rather than the tendency of such chains to display liquid crystalline phases which controls the dynamical mechanical behavior of such thermotropic polymers in the solid state. This contrasts to the case of liquid crystalline side chain polymers, where the socalled relaxation ,which involves the reorientation of the mesogenic group about one short axis ,is a characteristic property of the anisotropic state [6,7].

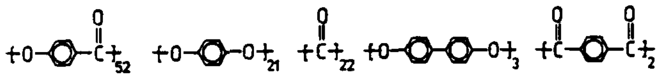
The paper is concerned with a discussion of relaxation properties of semiflexible and rigid chain molecules and a comparison of these properties with those found for flexible chain molecules. The experimental technique of choice is the determination of the complex shear modulus G^* at a frequency of 1 Hz within a temperature range from -150 °C up to 200 °C. Additionally, we performed studies on the dielectric relaxation properties of the same polymers with the aim to determine the activation diagrams of the relaxations .

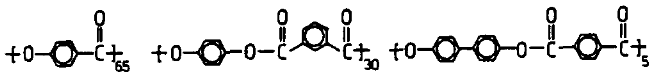
POLYMERS STUDIED

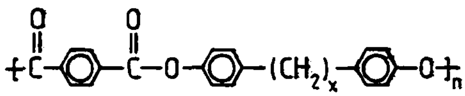
The studies were performed on two rigid chain molecules, the chemical structures of which are displayed in TABLE I. The polymers contain hydroxybenzoic acid as one comonomer unit. They are known to display a nematic phase at temperatures surpassing about 300 °C [8,9]. They are partially crystalline at room temperature. Unannealed samples posess a degree of crystallinity of about 20 to 25 %. The glass temperature is found from calorimetric studies to be about 110 °C for the case of polymer A and about 90 °C for the case of polymer B.

The semiflexible polymers C ,D and E contain identical mesogenic groups. The spacer length amounted to 6 (CH_2) - units in the case of polymer C, to 10 units in the case of polymer D. The copolymer E contained both spacer units with 10 and with 6 (CH_2) - units.The polymers are partially crystalline at room temperature,the degree of crystallinity amounting to about 35 to 40 %.(10).

TABLE I Chemical structure of the rigid chain and semiflexible chain thermotropic polymers

A 

B 

C,D,E 

The calorimetric investigations revealed that the crystalline regions melt at temperatures between 276 $^{\circ}$C(sample C), 262° C (sample D) and 260° C (sample E).The structural analysis of the high temperature phases failed,due to the low degree of thermal stability of the samples at temperatures surpassing 250 $^{\circ}$C.It is in any case a smectic phase and X-ray results as well as calorimetricx results indicate that these polymers display an ordered smectic phase.

The glass transition temperatures decrease only slightly with increasing length of the spacer units .They amounted to 70° C for polymer C, 65 $^{\circ}$C for Polymer D and 68° C for polymer E.

STRUCTURAL PROPERTIES

The X-ray data as well as the calorimetric data obtained for the rigid chain polymers reveal that the solid state displays some kind of three dimensional order.We were able to assign all X-ray reflections to an orthorhombic structure [8,9] The finding was ,however, that the chains are rotationally disordered about their long axis,while the centers of the chain elements are located on the three dimensional lattice.This causes the enthalpy and the entropy of the transition into the nematic phase to be extremely small,smaller by a factor of 10 to 20 in comparison to the corresponding values found for flexible chain molecules.In addition, we found that the crystals obtained by quenching are not in their equilibrium state,since the lattice constants vary continuously as a function of the annealing temperature and annealing time at constant volume of the unit cell.

The semiflexible chain molecules display an orthorhombic structure for the case of a spacer length of six methylene units and tetragonal structures in the case of the two remaining polymers.The lattice parameters are given below (TABLE II). The heats of transition and the enthalpies of transition are much larger than in the case of the rigid chain molecules

Table II Structural parameters of the semiflexible chain polymers C-E (see TABLE I)

Polymer	a(nm)	b(nm)	c(nm)	type
C	0.636	0.608	2.30	orthorh.
D	0.634	0.634	2.48	tetrag.
E	0.634	0.634	2.84	tetrag.

EXPERIMENTAL RESULTS

DIELECTRIC RELAXATION STUDIES

These studies were performed in order to detect the presence of relaxation processes and in order to determine their activation energy .The dielectric relaxation spectra are characterized by a low temperature relaxation,taking place in the temperature range between about -100 °C and 0° C both for the semiflexible as well as for the rigid chain molecules.Examples are shown in Figure 1 and Figure 2.

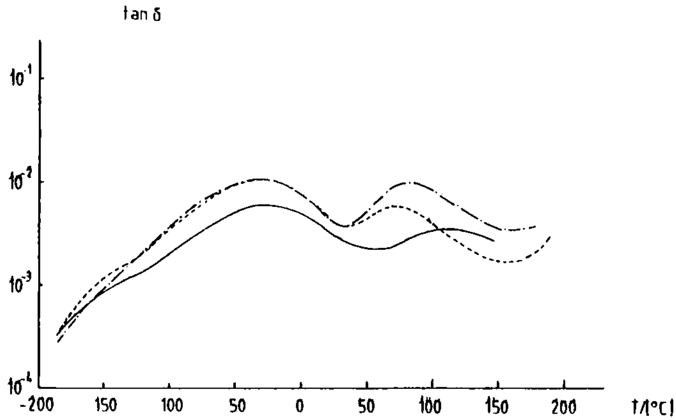


Figure 1 Dielectric loss of semiflexible chain molecule (—— C, – – D, –·– E)

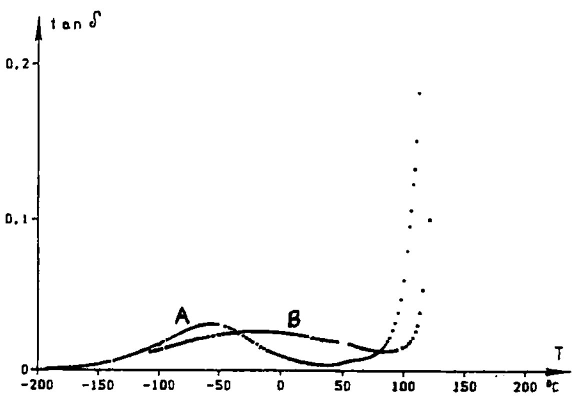


Figure 2 Dielectric loss of rigid chain molecules (A, B)

In addition one observes a relaxation at temperatures around 60 to 70 °C for the semiflexible chain molecules and betwenn 90 and

110 °C for the rigid chain molecules.These correspond to the glass transition.The low temperature process is a thermally activated process,as is obvious from the activation diagram whereas the high temperature process does not display a constant activation energy,as expected for a glass transition. The activation energies are of the order of 50 to 70 KJ/mol.So,the relaxation properties of the semiflexible and rigid chain molecules are characterized by two prominent relaxation processes,quite similar to the case of flexible chain polymers such as amorphous polycarbonate and partially crystalline poly (ethylene terephthalate).This holds both for the magnitude of the activation energy and for the temperature range in which these processes manifest themselves.In the following we will consider the way in which these relaxation processes couple to mechanical properties.

THE SHEAR MODULUS G

The observation is for the case of the two rigid chain polymers that the shear modulus G displays

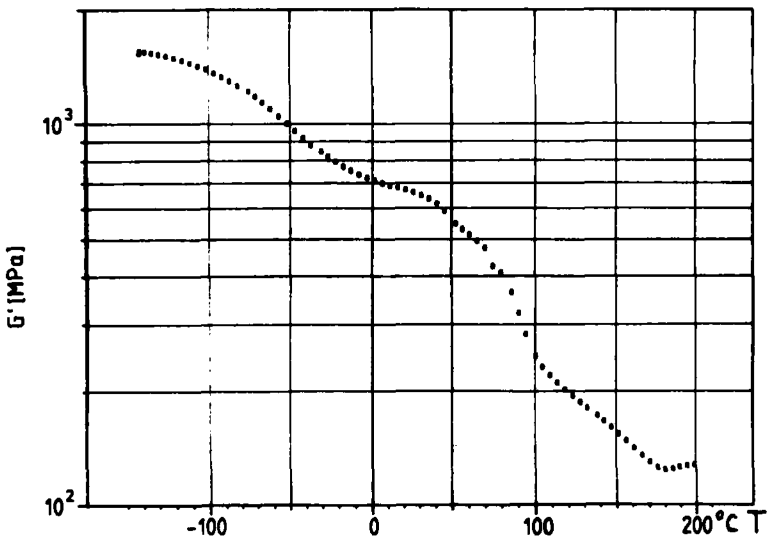


Figure 3 Torsional modulus observed for the rigid chain molecule A

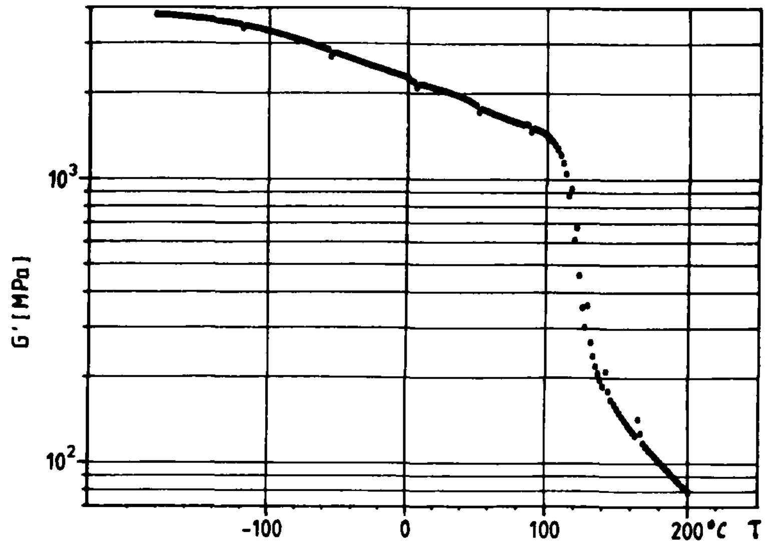


Figure 4 Torsional modulus observed for the rigid chain molecule B

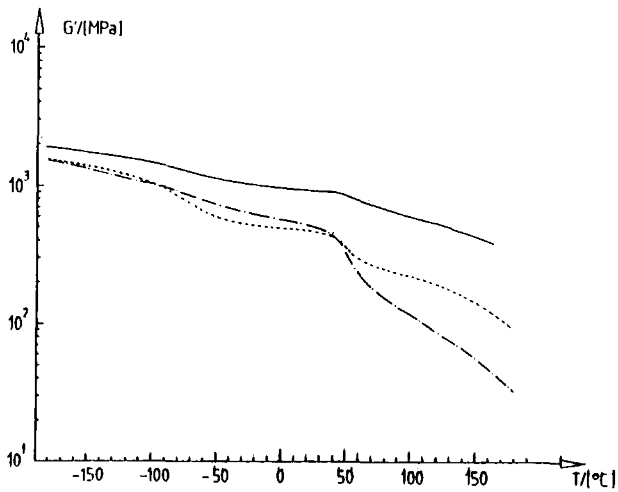


Figure 5 Torsional modulus observed for semiflexible chain molecules (—— C, — — D, —·—E)

two stepwise variations with increasing temperature which are obviously related to the onset of the ß-relaxation as well as of the relaxation (Figures 3,4) These stepwise variations of the storage modulus give rise to corresponding maxima for the loss moduli as well as for the loss tangent,which are similar to the ones observed for the dielectric properties.A similar behavior is observed in the case of the semiflexible chain molecules as is obvious from Figure 5 showing the temperature dependence of the modulus.Two distinct decays are observed in particular temperature intervals.

TENSILE MODULUS

The two relaxations taking place within the solid state both in the rigid chain polymers as well as in the case of the semiflexible chain molecules do not only couple to the shear modulus but also to the tensile modulus.A typical result obtained for the polymer is shown in Figure 6.

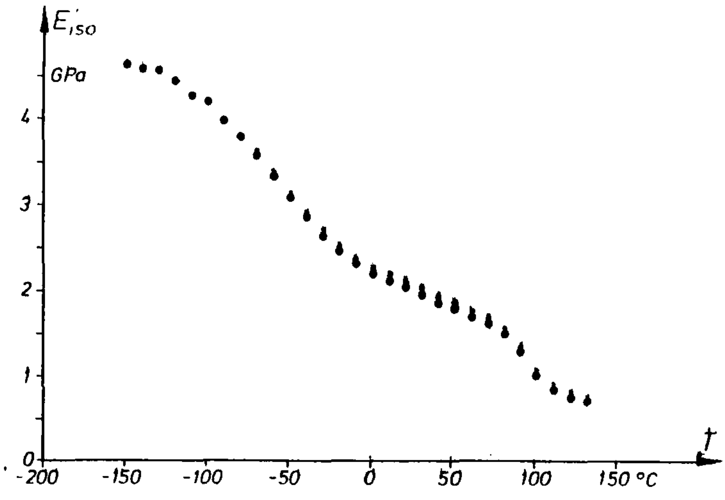


Figure 6 Tensile modulus obtained for the rigid chain polymer A

Again one observes a strong stepwise decrease of the storage modulus and a corresponding maximum for the loss modulus in the temperature range in which the two relaxation processes ,namely the and the β process take place.Similar variations of the tensile modulus have been observed for flexible chain polymers such as polycarbonate and poly (ethylene terephthalate)

DISCUSSION OF THE RELAXATION PROPERTIES

The obvious result of these studies is that both the semiflexible and the rigid chain polymers display secondary and primary relaxation processes which resemble those of flexible chain molecules. The presence of these processes gives rise to a strong decrease of the storage modulus.The activation energies as well as the characteristic temperature ranges are also quite similar to those found for comparable flexible chain polymers.So we will consider the absolute magnitudes of the storage moduli as well as the relaxation strength associated with the β and the glass relaxation processes and compare these values with the ones found for flexible chain molecules.

It is evident that the tensile modulus will be larger for rigid chain molecules in comparison to those found for flexible chain molecules.This becomes particularly obvious if we consider oriented samples and if we consider the tensile modulus parallel to the orientation direction.One result is displayed in Figure 7.

The tensile modulus is much higher than the one found for oriented flexible chain polymers ,in general.Nevertheless we observe that both the β as well as the process couple strongly to the modulus,causing it to decrease strongly already at temperatures far below room temperature.So the conclusion is that the tensile modulus will be much below the theoretical value at room temperature even for ideally oriented chain molecules,due to the presence of the β relaxation.

The shear moduli of semiflexible as well as of rigid chain molecules are found to be of the same order of magnitude as those of flexible chain molecules at low temperatures. The strong coupling of the ß relaxation to the shear modulus, particularly in the case of the polymer and of the polymer leads to a decrease of the modulus with increasing temperature which is much stronger than observed for many flexible chain polymers.

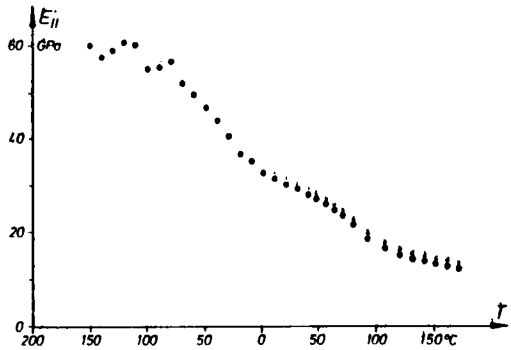


Figure 7 Tensile modulus E observed for highly oriented samples of polymer A

This is particularly evident from the relaxation properties of polystyrene, which display close to no secondary relaxation in the glassy state.

A particularly interesting result is obtained for the shear modulus at temperatures surpassing the glass transition temperatures. This causes the shear modulus of amorphous polymers such as PC and PMMA to decrease by at least 1 or 2 orders of magnitude. A much smaller decrease is observed for the shear modulus of the rigid chain molecules. The modulus is even found to be about constant for an extended range of temperatures in the case of the rigid chain polymer .

The semiflexible chain molecules display an even smaller decay of the modulus in this temperature range, particulary the semiflexible chain molecules containing only 6 spacer elements. It seems that the seggregation of the aromatic and aliphatic units within individual layers is one factor which contributes to the shear stability of the semiflexible polymers at elevate temperatures.A second factor is certainly the rather well developed crystalline structure displayed by the solid state.

The general finding is thus that semiflexible and rigid chain molecules display a rather strong secondary relaxation process which is directly related to the chemical structure of the mesogenic units along the chain backbone.These give rise to a substantial decrease of the storage modulus already at temperatures well below room temperature.The details of the relaxation properties characteristic of the low temperature process are obviously controlled by the chain rigidity and the length of the spacer units.The high temperature glass process seems to couple less strongly to the dynamical mechanical properties in the case of the rigid and particularly the semiflexible chain molecules in comparison to the case of flexible chain molecules.

REFERENCES

1. N.G.McCrum,B.E.Read,G.Williams,Anelastic and Dielectric Effects in Polymers Solids (Wiley,New York,1967)
2. I.M.Ward,Mechanical Properties of Solid Polymers (Wiley,New York,1983)
3. A.Cifferi,W.R.Krigbaum,R.B.Meyer Polymer Liquid Crystals (Academic Press,New York,1982)
4. A.Blumstein,Liquid Crystals and Ordered Fluids (Plenum Press,New York ,1985)
5. Adv.in Polym.Sci 60,61,Liquid Crystal Polymers(Springer Verlag,Heidelberg ,1984)
6. H.Kresse,V.P.Shibaev,Makromol.Chem.Rapid Commun.,5,63 (1984)
7. R.Zentel,G.R.Strobl,H.Ringsdorf Macromolecules,18,960 (1985)
8. J.H.Wendorff,H.J.Zimmermann Angew.Makromol.Chem.,145/146,227 (1986)
9. H.J.Zimmermann,PhD-Thesis,TH Darmstadt (1987)
10. G.Frick,Master-Thesis,TH Darmstadt (1987)