Polymer Bulletin 27, 221–226 (1991)

Polymer Bulletin

Mesophase elastomers: Stress-induced mesophase formation in poly(diethylsiloxane) networks and their thermomechanical behaviour

Yu. K. Godovsky* **and L. A. Valetskaya**

Karpov Institute of Physical Chemistry, Ul. Obukha 10, SU-103064 Moscow, USSR

Dedicated to Prof. Dr. H. G. Zachmann on the occasion of his 60-th birthday

Summary

The length-temperature dependence for the mesophase PDES elastomers loaded with a constant force has been studied with particular emphasis on the temperature interval of the mesophase stability as a function of force (extension). Although this behaviour is qualitatively similar to the stress-induced crystallization of elastomers, there is a large quantitative difference resulting from rather small enthalpy changes during the stress-induced mesophase formation in PDES elastomers. Such a behaviour is well predicted by thermodynamics. It is shown that, in contrast to the stress-induced crystallization, as a result of the very large stress-temperature coefficient of the mesophase induced during stretching, the self-reinforcing effects in mesophase elastomers may arise at high temperatures.

Introduction

Attaching conventional mesogenes via flexible spacer to a flexible linear polymer and subsequent crosslinking provides an approach for obtaining side chain liquid-crystalline elastomers showing both rubber-like behaviour and liquid-crystalline properties (1,2). Such elastomeric materials are of considerable interest both from scientific and practical points of view, first of all due to their interesting thermoelastic and optical properties. On the other hand, recently have been developed a new class of polymers which are able to form thermotropic mesophases without any mesogenes neither in the main chain nor in the side gropus of the macromolecule (3,4). In the most striking form the tendency to build up such mesophases is displayed by polymers with flexible inorganic backbones, such as polyorganosiloxanes and some polyphosphazenes. From the structural point of view these mesophases in flexible polymers can reasonably be regarded as highly disordered crystals with a high level of molecular mobility (3). In linear polyorganosiloxanes the temperature range of mesophase stability depends drastically on the length of the side chains. While in the high enough molecular weight noncrosslinked poly(diethylsiloxane) (PDES) the temperature interval in which the mesophase can exist is normally of approximately 290-320 K, the temperature interval of the mesophase stability in poly(dipropylsiloxane) of high enough molecular weight increases considerably being 333-479 K (5). The degree of mesophasity and the temperature of isotropization diminish considerably after crosslinking of PDES. Investigation of the mechanical properties of the model crosslinked PDES networks, either initially amorphous or mesophase, revealed some interesting features of the stress-strain behaviour and of the heat and energy effects accompanying the stretching of the PDES films in the stretching calorimeter (6,7).

---

*To whom offprint requests should be sent

The interesting aspect of the behaviour of PDES networks is the stress-induced mesophase formation during uniaxial stretching of amorphous film. The cyclic deformations of such networks are accompanied by large hysteresses effects resulting from the stress-induced mesophase formation on stretching followed by the immediate isotropization during contraction. As it has been emphasized in previous publications (8,9) there is a certain analogy between the stress-induced mesophase formation in PDES networks and the stress-induced crystallization upon uniaxial stretching of crystallizable polymer networks. These processes are accompanied by self-reinforcing of the stretched samples. However, the simple thermodynamic analysis given below predicts a very important difference between these processes concerning the temperature of isotropization during heating of stressed samples. According to the thermodynamic analysis (10), in the phase transition accompanied by a change in length, the relationship between force (f) and temperature T, is given by

$$[d(f/T)/d(1/T)]_p = \Delta H/\Delta L \qquad (1)$$

where ΔH and ΔL are the changes in enthalpy and length, respectively, which occur during fusion of the stretched elastomer at constant T, p, and f. Normally $\Delta L < 0$, whereas $\Delta H > 0$. Therefore according to Eq.(1), f/T will increase with T. It means that the temperature of the phase transition increases with an increase in the applied tensile force at constant pressure. During melting of stretched crystalline networks or isotropization of stretched mesophase networks the length of the sample decreases, however, some times (supercontraction), in both cases due to melting of the oriented crystallites or mesophase domains, which leads to a large change in length. But, ΔH_i of isotropization is at least one order of magnitude smaller than the heat of fusion, ΔH_m. Therefore, according to Eq.(1) the force coefficient of the temperature of transition should be at least one order of magnitude higher for the isotropization of the mesophase elastomers in comparison with the melting of the stretched crystalline networks. For the stress-induced crystallizable networks the increase of the melting temperature can reach 10-30°C, depending on the degree of extension (10). It means that for the stretched mesophase elastomers the isotropization temperature may be a hundred degrees higher than for the same elastomer in the nonstretched state. Therefore, in the stretched mesophase elastomers a self-reinforcing mechanism can exist even at very high temperatures.

In this paper the results concerning the thermomechanical behaviour and isotropization of stretched mesophase PDES elastomers are presented with the particular emphasis on the predicted effect and compared with the behaviour of common crystallizable elastomers.

Experimental

Samples: The samples were cut from the films of crosslinked PDES. The films were high molecular weight PDES vulcanized with 2 wt.% ethylsilicate (6). The typical dimensions of the samples were (30-50)x5x1 mm^3.

Thermomechanical measurements: There are two experimental approaches to check the predicted effect: force-temperature and length-temperature measurements. Our thermomechanical study was made by carefull measuring (by means of a cathetometer) the length of the samples as a function of temperature while the samples supported a constant load. The sample loaded with a given load at room temperature was placed in the thermostat and after its length reached a constant value at room temperature the measurements started.

The measurements were conducted in two modes . In one mode the sample was heated with the heating rate of about 1 °C/ min . In the second mode the temperature was changed step by step. Both modes gave self-consistent results. Some experiments were executed in the regime of heating-cooling cycles to follow the mesophase formation during cooling of the stretched samples. The shrinkage during isotropization was very large and rather sharp, the sharpness of the shrinkage being a good manifestation of the cooperative character of the phase transition. The influence of stress (extension ratio) on the transformation temperature has also been investigated in similar experiments under various loads.

Finally, some experiments were executed below room temperature to follow the changes which occur in the vicinity of crystal-crystal transformation and melting. In this case after a given stretching of the sample with a constant load at room temperature, it was placed in a cryostat and cooled down to low temperatures. Then the sample was reheated with a heating rate of about 1°C/min to room temperature with simulteneous measurements of the length of the sample.

Results and discussion

Fig.1 shows the results of the thermomechanical measurements for the studied PDES elastomer. Although during the experiments the sample length L at constant force was measured as a function of temperature, it is more convenient for the purposes of comparison to indicate the initial extension ratio corresponding to this force. A well pronounced stress-induced mesophase appeared in the studied samples normally after an extension of approximately to 1.7-1.9.

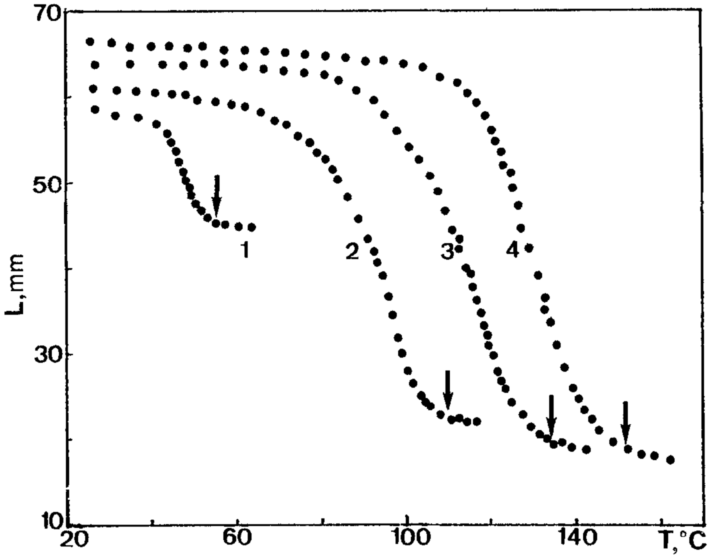

Figure 1:Length under various loads (various extension ratios) vs. temperature for mesophase PDES elastomers. The respective values of the extension ratios are:1 - 1.92; 2 - 3.10; 3 - 3.95; 4 - 4.53. Arrows indicate the isotropization temperature T_i

As it is seen from Fig.1 the shrinkage of samples is very small in the initial temperature range. With rising temperature it increases, however, progressively and finally the supercontraction occurs. Dependence of the temperature of the supercontraction on the extension ratio is extremely large. The temperature at which the supercontraction of the sample is finished was chosen as the isotropization temperature, T_i.

Fig.2 shows the dependence of T_i on the extension ratio. It is linear one in the range of the extension ratios studied. In the temperature range above the isotropization temperature T_i, is observed the thermomechanical behaviour typical for a rubber. The length of the sample is linearly dependent on temperature with a negative thermal expansivity of the order of 10^{-3} K.The $dTi/d\lambda$ coefficient is in the range of extension ratios $\lambda > 2$ of 33 K per 100 %. Extrapolation to zero force (extension) gives $T_i = 17 \pm 2^oC$ which is very close to the values obtained by DSC for the non-stretched samples, as well as to that obtained during heating of the cooled sample (see Fig.4).

The effect of contraction of the mesophase samples is quite reversible because during cooling of the loaded isotropic samples the oriented mesophase occured again spontaneously. This is well confirmed in Fig.3, where are shown the first three succesive heating-cooling cycles. Although there are some small differences relative to the characteristic temperatures of the repetitive contraction and elongation steps, the general picture is quite reproducible. It is remarkable that the degree of undercooling at which the spontaneous elongation occurs in all runs is of about $\Delta T = 20\text{-}25^oC$. The superelongation after the first cycle is somewhat larger than in the first one, which seems to mean that the mesophase induced at high temepratures during cooling of the loaded samples is more perfect than that induced at room temperature during stretching.

Fig.4 shows the thermomechanical behaviour of the sample which after loading at room temperature (the degree of deformation was approximately 250 %) was cooled under load

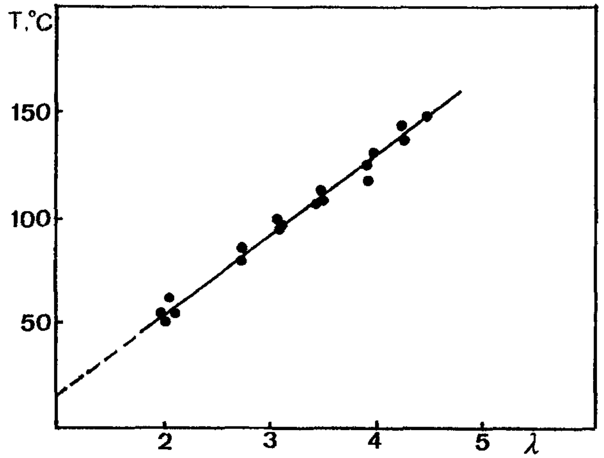

Figure 2: Isotropization temperature, T_i, vs. extension ratio, λ, for mesomorphic PDES elastomers

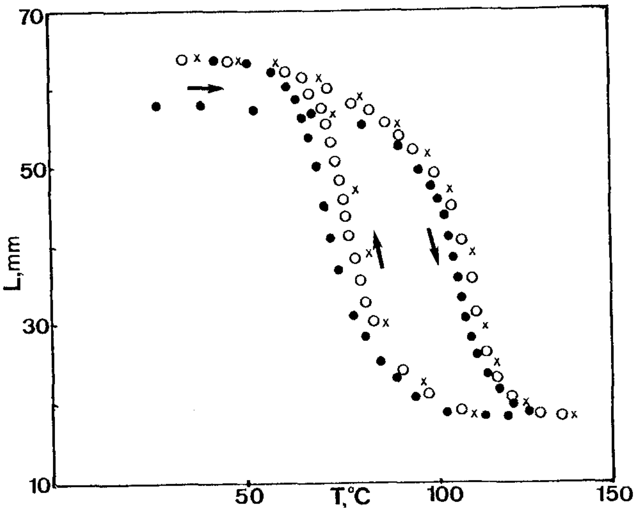

Figure 3: Reversible contraction and spontaneous elongation of mesomorphic PDES elastomers during heating-cooling cycles. O - 1-st run; O - 2-nd run; x - 3-rd run

with a cooling rate of about 1 ^{o}C/min to -80 ^{o}C and then reheated to room temperature in the loaded state with the similar heating rate. It is evident that no changes occur in the length of the sample in the vicinity of -60 ^{o}C, where in the nonstretched samples normally the crystal-crystal transformation is observed. In the vicinity of melting takes place only a small elongation during cooling and a similar shrinkage during heating. Similar experiments were also performed in a somewhat different manner. After cooling the loaded sample to -80 ^{o} C the load was removed. Because the sample is solid at this temperature, no contraction occurs after removing the load. Then the sample was heated with the same heating rate to room temperature. In this case similar changes in length of the sample occurs in the vicinity of the crystal-crystal transformation and melting while the supercontraction typical for isotropization, in contrast to the loaded sample, started immediately after melting. Thus the final isotropization of the sample occured in the vicinity of room temperature like in the non-stretched samples.

Conclusion

The thermomechanical behaviour of the mesomorphic PDES elastomers can be summarized as follows. Although qualitatively the stress-induced mesophase formation in PDES elastomers and their thermomechanical behaviour resembles the stress-induced crystallization of polymer networks, there is a very large quantitative difference, resulting from the large difference between the enthalpy changes of the both processess. The temperature coefficient of the stress-induced mesophase stability is one order of magnitude higher than the corresponding coefficient of the stress-induced crystallization. This difference in the thermo-mechanical behaviour is well predicted by the Eq.(1). The consequence of this difference may be of a great practical importance. It is well known that the stress-induced crystallization in elastomers, in particular in NR, leads to a considerable increase of the modulus of elasticity and other mechanical properties due to the appearence of the rigid crystallites which serves as fillers. However, the stress-induced crystallization in elastomers appears normally only some dozens degrees above the melting point of the non-stretched sample. The mesomorphic crystallites arising in the mesophase elastomers due to the stress-induced mesophase

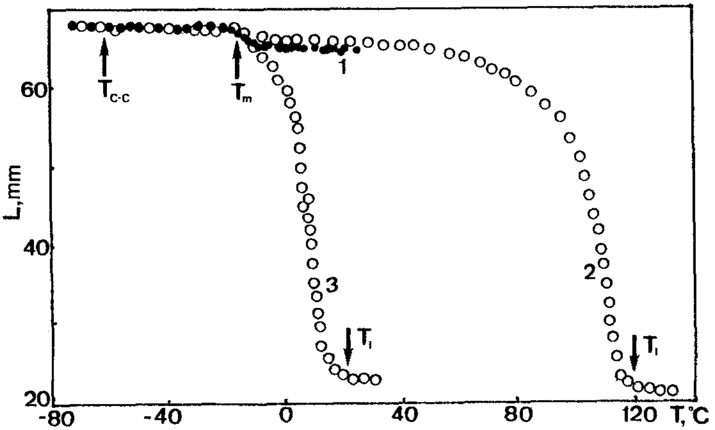

Figure 4: Length as a function of temperature for mesomorphic PDES elastomers. 1 - cooling under constant force 1.7 N (λ = 3.38); 2 - heating under the same force; 3 - heating under zero force. $T_{c\text{-}c}$ is the temperature of crystal-crystal transition; T_m is the melting temperature; T_i is the isotropization temperature

formation also serve as fillers and their appearence also results in improvement of mechanical properties. However, the self-reinforcing effects in the mesophase elastomers can arise at considerably higher temperatures relatively to the isotropization temperature of isotropic samples. In particular, in PDES elastomers we followed the stress-induced mesophase formation and corresponding self-reinforcement effects at temperatures more than a hundred degrees above the isotropization temperature.

Acknowledgment

This work was completed during the visit of Yu.K.Godovsky as visiting professor to Institut für Makromolekulare Chemie, Universität Freiburg.

We greatfully thank Prof. Dr.R.Mühlhaupt for his invitation and the SFB 60 of the Deutsche Forschungsgemeinschaft within the SFB 60 for financial support.

References

1. Gleim W, Finkelmann H, in *Side Chain Liquid Crystal Polymers*, C.B.McArdle, ed.,Blackie, Glasgow and London, 1989, p.287
2. Zentel R (1989) Angew Chem Adv Mater 101: 1437
3. Godovsky YK, Papkov VS (1989) Adv Polymer Science 88: 129
4. Godovsky YK,Papkov VS (1986) Makromol Chem, Macromol Symp.4: 71
5. Godovsky YK, Mamaeva II, Makarova NN, Papkov VS, Kuzmin NN (1985) Makromol Chem, Rapid Commun 6: 797
6. Godovsky YK, Volegova IA et al (1988) Vysokomol Soedin A30: 359
7. Papkov VS, Godovsky YK et al (1989) Vysokomol Soedin A31: 1577
8. Papkov VS, Kvachev YP (1989) Progr Colloid Polym Sci 80: 221
9. Godovsky YK, Valetskaya LA, Papkov VS, III European Polymer Federation Symposium, Makromol Chem Macromol Symp (to be published)
10. Mandelkern L (1964) *Crystallization of Polymers* McGraw, N.Y, Ch.7

Accepted August 24, 1991 C