EFFECT OF STRUCTURIZATION IN OLIGOMERS ON THE TEMPERATURE CHARACTERISTICS OF THEIR THERMOPHYSICAL PROPERTIES

L. A. Sukhareva, P. I. Zubov,
and G. N. Yashchenko

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Results are shown of a study concerning the effect of oligomer block length and flexibility on the temperature characteristics of thermophysical properties, on the internal stresses, and on the structural transformations of oligomer systems.

It has been discovered in a study concerning the thermophysical properties of oligoether maleinates [1] that the variation in thermophysical properties with an extremum within a certain temperature range is due to slower relaxation processes and the formation of a lattice structure of associated oligomer molecules.

In this study the authors were concerned with the effect of oligomer block length and flexibility on the temperature characteristics of their thermophysical properties, on their internal stresses, and on the structural transformations of oligomer systems.

We studied oligocarbonate methacrylates [2] with a regular distribution of active functional groups of varying lengths and flexibility: blocks of bi-(methacryl-oxyethylene carbonate) ethylene glycol (MOCEG), bi-(methacryl-oxyethylene carbonate) butylene glycol-1,4 (MOCEB), bi-(methacryl-oxyethylene carbonate) hexamethylene glycol-1,6 (MOCHG), and bi-(methacryl-oxyethylene carbonate) diethylene glycol (MOCDG).

The thermophysical properties were studied over the temperature range from —180 to +100°C by the adiabatic-shell method under quasisteady thermal conditions [3]. Liquid oligomers were poured into a quartz jar in the shape of a hollow cylinder: inside radius 11.5 mm, outside radius 13.0 mm, and height 100 mm. The polymer specimens cast and cured in this manner had the same dimensions. The thermophysical properties were determined within a ±5 to 10% accuracy. The internal stresses were examined by the optical-polarization method throughout the same temperature range. The effect of temperature on the structural transformations of oligomer systems was examined by the rheological method with a Shvedov apparatus comprising two coaxial cylinders as well as by infrared spectroscopy with a model UR-20 spectrophotometer.

The variation in the thermal conductivity, the thermal diffusivity, and the specific heat of oligocarbonate methacrylates over a wide temperature range is shown in Fig. 1. It is quite evident that the thermal conductivity of an oligomer is not a monotonic function of the temperature; it reaches an extremum at some temperature which depends on the structure of the oligomer block. For a longer and more flexible oligomer block this maximum increases and shifts toward lower temperatures, while the area under the temperature curve within that range also increases. Within that range one also notes inflection points on the temperature curves of thermal conductivity.

The formation of a spatial lattice in oligomer coatings, as a result of chemical bonds produced during polymerization at 80°C, shows no substantial effect on the trend of these temperature characteristics.

Fig. 1b is shown the effect of temperature on the thermophysical properties of lattice polymers formed from oligomers with various block structures. Evidently, the thermophysical properties of polymers with spatially interlinked chemical bonds are also not monotonic functions of the temperature: their temperature characteristics pass through maxima and inflections.

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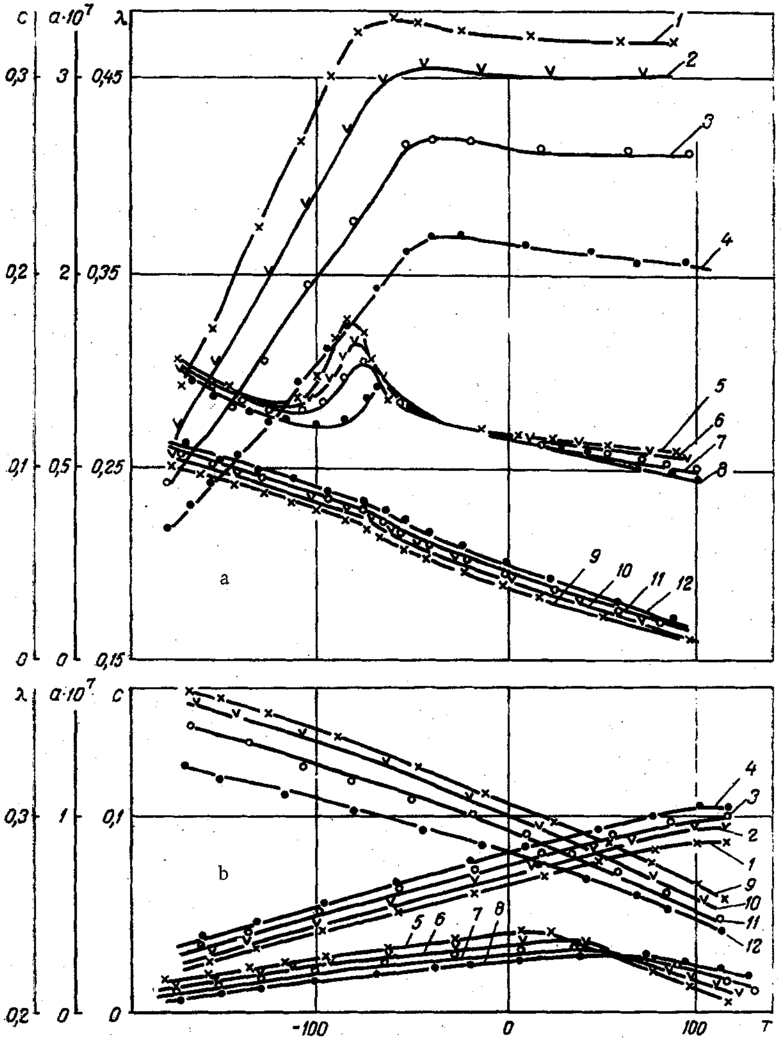

Fig. 1. Temperature characteristics of the thermophysical properties: a) oligocarbonate methacrylates; b) lattice polymers formed at 80°C; 1, 2, 3, 4) c (kJ/kg · °C); 5, 6, 7, 8) λ(W/m · °C); 9, 10, 11, 12) a(m^2/sec); 1, 5, 9) MOCDG; 2, 6, 10) MOCHG; 3, 7, 11) MOCBG; 4, 8, 12) MOCEG; temperature T(°C).

Unlike the case of oligomers, these special values occur near the glass-transition temperature and they are associated with a partial breakdown of the lattice structure during the transition of a polymer to its super-elastic state (Fig. 1b). For longer and more flexible oligomer blocks the maximum thermal conductivity shifts toward lower temperatures, following a change in the glass-transition temperature.

In order to explain the causes of this amonotonic trend, we examined the effect of the oligomer block structure on the rate of relaxation processes within the same temperature range, estimating this effect on the basis of the internal stresses. The temperature characteristics of the internal stresses are shown in Fig. 2 for oligomers with various block structures (curves 4-6) and for respective oligomer-based coatings (curves 1-3). As the temperature of an oligomer decreases to —10 and —20°C, there appear internal stresses in the system which buildup linearly until they reach a constant level at a temperature corresponding to the maximum values of the thermophysical properties. In a longer and more flexible oligomer block the stresses extend to the surface and reach their limits at lower temperatures.

The internal stresses in spatially interlinked polymers, as a function of the temperature, follow an analogous trend. At a temperature above the glass-transition point the internal stresses relax almost completely. As the temperature decreases, the stresses increase to their limit at a temperature corresponding to the maximum values of the thermophysical properties of the respective oligomer, and beyond which they remain essentially constant.

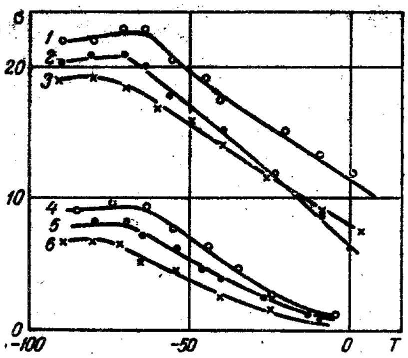

Fig. 2. Internal stresses σ (kg /cm^2) as a function of the temperature T(°C), for oligomers (curves 4, 5, 6) and for respective oligomer-based coatings formed at 80°C (curves 1, 2, 3): 1, 4) MOCEG; 2, 5) MOCBG; 3, 6) MOSDEG.

The monotonically decreasing thermal conductivity and thermal diffusivity of spatial-lattice polymers, as well as the absence of any special points within the low-temperature range of their characteristics, are apparently related to an appreciable slowdown of the relaxation processes and to the lower mobility of structural components in this temperature range. About the glass-transition temperature, on the other hand, complete relaxation in the system is prevented by a breakdown of bonds between structural components of a spatial lattice as well as by a higher mobility of these components, accompanied also by an extremal trend of the thermophysical properties.

The appearance of internal stresses in an oligomer system and their buildup to a constant limit can be attributed to the formation of a lattice structure by the associated oligomer molecules.

The maxima in the low-temperature range of thermophysical properties, in the case of oligomers, are probably a consequence of incomplete relaxation in an oligomer lattice with high-mobility structural components and formed by physical bonds — unlike the lattice of spatially interlinked polymers. In order to verify this hypothesis, we have studied the effect of temperature on the rheological properties of oligomer blocks of varying flexibility.

The viscosity as a function of the shearing stress in oligocarbonate methacrylates is shown in Figs. 3 and 4 for various temperatures. The MOCEG oligomer with shortest and most rigid blocks (Fig. 3a) represents a system which is weakly structurized within temperatures from +20 to —15°C.

As the temperature decreases, the viscosity of the system increases fast and without any significant change in the trend of the rheological curves. This indicates that a decrease in the temperature of such a system is not followed by a substantial aggregation of structural components. Under these conditions, apparently, the formation of a lattice structure is effected as a result of local physical bonds between the original structure components.

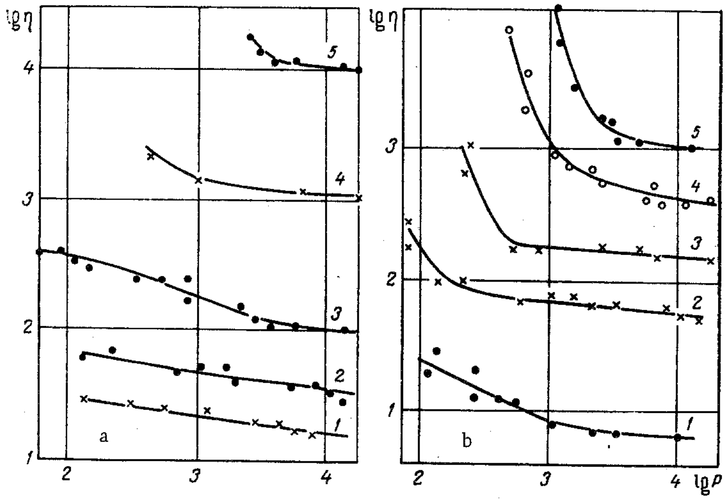

Fig 3. Logarithm of the viscosity versus logarithm of the shearing stress: a) for MOCEG at: 1) +10°C; 2) 0°C; 3) —15°C; 4) —25°C; 5) —40°C; b) for MOCDG at: 1) +10°C; 2) —10°C; 3) —27°C; 4) —40°C; 5) —50°C.

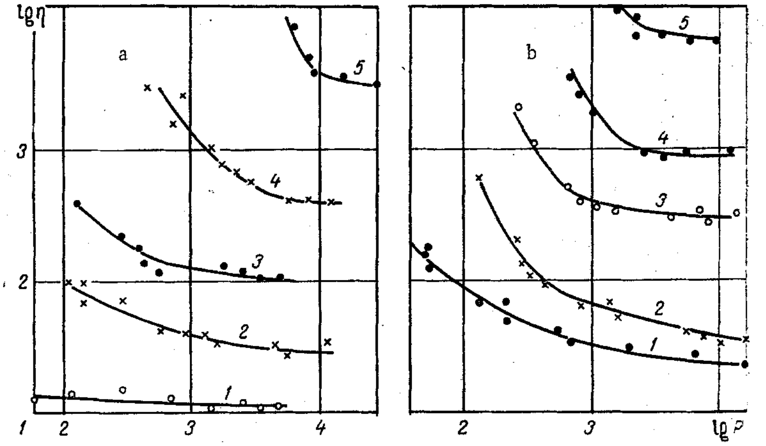

Fig. 4. Logarithm of the viscosity versus logarithm of the shearing stress: a) for MOCBG at: 1) +10°C; 2) —10°C; 3) —30°C; 4) —40°C; 5) —60°C; b) for MOCG at: 1) +10°C; 2) —20°C; 3) —30°C; 4) —45°C; 5) —55°C.

The temperature characteristics of the rheological properties follow a different trend in the case of the MOCDG oligomer with a more flexible block (Fig. 3b). MOCDG is more structurized at —15°C than MOCEG. As the temperature decreases further to —30 and —150°C, the difference between the viscosity of a broken down structure and that of a retained structure will increase; at the same temperature, moreover, the viscosity of a broken down MOCDG structure is by two decimal orders of magnitude lower than the viscosity of a MOCEG structure. This is, apparently, due to an aggregation of structural components with an accompanying temperature drop and a subsequent formation of a lattice from large supermolecular structures.

With regard to the effect of temperature on their rheological properties, MOCEG and MOCDG rank as intermediate between rigid and flexible oligomer blocks in our study here. As the temperature decreases, the MOCEG oligomer structurizes weakly (Fig. 4a) and the temperature characteristic of its rheological properties approaches that of the MOCDG oligomer.

The structurization of oligocarbonate metacrylates at various temperatures from +50 to —100°C was examined by infrared spectroscopy. Some shift of the absorption bands has been detected, corresponding to oscillations of the various functional groups, with a simultaneous change in the intensity of these bands.

Thus, the frequency of the absorption band corresponding to antisymmetric valence oscillations in methylene groups decreased during cooling from 2938 to 2928 cm^{-1} in the case of MOCDG and from 2945 to 2933 cm^{-1} in the case of MOCEG. The relative intensity of these bands increased at the same time by approximately 30%. These changes occurred essentially while the temperature of MOCDG dropped to —80°C and the temperature of MOCEG dropped to —65°C, a further drop to —100°C produced neither a further shift nor a higher relative intensity of the absorption band for methylene groups. According to [4], these results may be regarded as evidence that hydrogen bonds are formed by methylene groups.

Within the range of valence oscillations in C—O groups at about 1175, 1040, and 1275 cm^{-1}, the intensity of the absorption bands for all specimens increased somewhat during cooling down to —60 and —80°C, while further cooling down to —100°C was followed by an appreciable decrease in the intensity. This is, apparently, related to a somewhat changing lengths of bonds in a molecule during the transition of a polymer to solid state, when the derivative of the dipole moment changes and this causes a change in the intensity of the absorption bands.

During cooling through the test range of temperatures, the relative intensity of the absorption bands corresponding to valence oscillations in $C=C$ groups at about 1660 cm^{-1} increased more significantly than for any other functional groups in the system. While for MOCDG this increase ceased at about —80°C, for MOCEG it ceased already at about —65°C. Further cooling down to —100°C did not produce a further change in the relative intensity. This is characteristic of that given group for which the intensity of the absorption band depends largely on the configuration of adjoining functional groups [6] and, therefore, on the configuration of the entire macromolecule.

NOTATION

T	is the temperature, °C;
λ	is the thermal conductivity, W/m · °C;
a	is the thermal diffusivity, m^2/sec;
c	is the specific heat, kJ/kg · °C;
σ	are the internal stresses, kg/cm^2;
$(\log P)$	is the logarithm of the shearing stress;
$(\log \eta)$	is the logarithm of the viscosity.

LITERATURE CITED

1. L. A. Sukhareva, G. N. Yashchenko, and P. I. Zubov, Vysokomolek. Soedn. (1973).
2. A. A. Berlin, Yu. M. Sivergin, T. Ya. Kefeli, N. L. Marshavina, N. B. Mirenskaya, and E. S. Alimpieva, Vysokomolek. Soedn., 13, 2676 (1971).
3. L. L. Vasil'ev, S. A. Tanaeva, and A. D. Shnyrev, Inzh. Fiz. Zh., 17, No. 6 (1969).
4. Aksnnes and Songstad, Acta Chem. Scand., 18, 655 (1964).
5. A. Z. Gadzhiev and I. S. Pominov, in: Application of Molecular Spectroscopy to Chemistry [in Russian], Izd. Nauka, Moscow (1966).
6. L. Bellami, Infrared Spectra of Compound Molecules [Russian translation], Moscow (1963).