Heat Pulse Monitoring of Curing and Polymer–Gas Systems

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SYNOPSIS

An implantable thermal probe is used to study the reaction of molten polymers and curing systems to pulse heat release. At the heating rates $\dot{T} \geq 5 \cdot 10^5$ K/s, a polymer system shows the response to pulse heating that is confined in time and reproducible with respect to temperature. This response is related to the abrupt change in the conditions of the contact between the probe and a substance. The temperature of the response T^* is determined by the polymer properties and depends on the pressure and $\dot{T}$. The pulse thermal probe method, which includes two measuring procedures, complementing each other, has been used to monitor a number of processes in polymeric systems. The variation of the values of T^* and the thermal activity of a polymer is compared with the variation of its molecular weight ($\bar{M}_n \sim 10^2$–10^6), the molecular weight distribution, and the concentration of a low molecular weight component. The method allows one to trace the kinetics of polymerization and curing and the kinetics of dissolution of volatile impurity and polymer devolatilization, and to determine the limit of supersaturation of gas solutions in molten polymers. The pulse repetition frequency is changed from 0.1 to 1 Hz. The heated volume of a substance is 10^{-4} mm^3. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The methods of the study of the substance properties and characteristics of processes based on the recording and analysis of the system response to some perturbation (mechanical, acoustic, electrical) have found a wide application for polymers.[1] We used for these purposes the method of pulse heating of a substance on the surface of a wire probe[2,3] and revealed the response confined in time and reproducible with respect to temperature of a polymeric system to heat release. The nature of this response is related to an abrupt violation of the conditions of the probe contact with a substance. The temperature of the response depends on the instantaneous composition and physicochemical properties of a substance. Its value is above the traditional temperature range for experiments with polymers. By the character of the response, the observed phenomenon is similar to that of spontaneous nucleation in superheated low molecular weight liquids.[2] We shall conventionally take the response temperature T^* for the temperature of the attainable superheat of a polymer system. The phenomenon of the attainable superheat of polymers and the kinetics of the onset of a vapor phase have recently attracted the attention of investigators and have been studied for systems of polymer–solvent[4–9] and for polymer melts[8–10] and elastomers.[11]

In the present work, we shall not consider the peculiarities characteristic of the superheated states of polymers (see Refs. 7–11), but shall discuss the possibilities of the practical use of the method of pulse heating for the evaluation of a number of parameters of polymeric systems and processes, in particular, the value of the molecular mass and polydispersity, kinetics of curing, kinetics of dissolution or removal of volatile impurities, and the boundaries of the stability of a condensed state of an oligomer supersaturated with a gas. The prospects of effective use of the method are based on its speed, microquantity of the analyzed substance, independence of the observed parameter (T^*) on the medium temperature, and compactness and noise im-

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munity of the equipment employed. The characteristic time of heating is of the order of 10^{-4}–10^{-5} s, and the heated volume is of the order of 10^{-4} mm^3. The pulse repetition rate is determined by the relaxation rate of the region of the probe–substance contact, and in our experiments, it was from 0.1 to 1 Hz. To monitor the process of relaxation, we used an auxiliary technique measuring the change in thermal activity of substance at the probe surface layer. At the same time, data on the kinetics of changes in thermal activity of a responding system are of independent interest. The combination of two techniques within the framework of one experiment allows one to make more reliable conclusions on the character processes under study.

SUPERHEAT AND THERMAL ACTIVITY OF LIQUIDS

It is convenient to consider the phenomenon of superheat, which is a particular case of supersaturation of a substance, for the boiling of a low molecular weight liquid. Usually, boiling begins on ready evaporation centers at a small superheat $\Delta T = T - T_s$, where T_s is the temperature of the liquid–vapor equilibrium at a given pressure. By reducing the volume of a system and the time of its transition into a metastable state, one can exclude ordinary boiling and achieve high values of ΔT. In this case, the relaxation of a system occurs via spontaneous nucleation. In this regime, the threshold mechanism of boiling becomes apparent because of the extremely strong temperature dependence of the nucleation rate. This ensures the reproducibility of the temperature of intensive spontaneous boiling at a given pressure. This temperature is taken for the temperature of the attainable superheat of a liquid T^*. Its value is determined mainly by the surface tension and the vapor pressure in a critical bubble. Values of T^* for different low molecular weight liquids measured by various methods are consistent with the results of calculations based on the homogeneous nucleation theory.[12,13] As an example, Figure 1 shows the region of superheated states in the phase diagram of a toluene–polystyrene system.

Thermal activity characterizes the medium assimilation to heat release in an unsteady process and is given by $b = (\lambda \rho c)^{0.5}$, where λ, ρ, and c are the thermal conductivity, the density, and the heat capacity of the medium, respectively. Thermal activity influences the temperature field change in time for values of the Fourier criterion $F_0 = a\tau/d^2 < 0.5$. Here, a is the thermal diffusivity of the medium; τ,
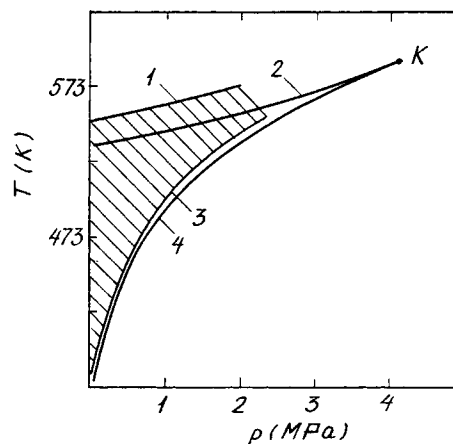
Figure 1 Phase diagram for toluene and for 50 wt % polystyrene/toluene solution: (1, 2) $T^*(p)$ curves for the solution and the pure solvent accordingly (our data); (3, 4) $T_s(p)$ curves for the samples.[6] K is the critical point of toluene. The superheated-state region of the solution is crosshatched.

the heating time, and d, the characteristic size of a heater.

EXPERIMENTAL

Apparatus and Procedure

The main element of the measuring circuit is a wire probe immersed in a liquid under investigation. The probe diameter d is $2 \cdot 10^{-5}$ m, the length l is about 1–2 cm, and the material is platinum. The probe serves simultaneously as a heater and as a resistance thermometer. The idea of the method is based on the high sensitivity of the probe to the change of the conditions of heat transfer to a liquid due to the large ratio of the probe surface area to its volume. In the course of T^* measurements, a record is made of the moment of the abrupt violation of the contact conditions in the process of heating. In the course of the time-interval measurements (the auxiliary technique), the variation of the thermal activity (from pulse to pulse) of the substance is tracked. We shall consider consecutively both these types of measurements.

Method of T^* Determination

The probe is connected to the bridge circuit; it is heated by a potential pulse from a generator G1 (see Fig. 2). The pulse length is $\tau \sim$ 10–100 μs, and the amplitude is of the order of 10 V. The substance contacting with the probe is also heated. The pulse
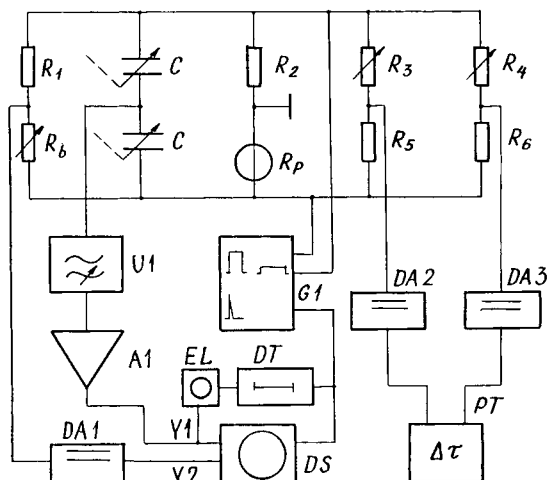
**Figure 2** Block diagram of the apparatus: R_p, probe; R_b, resistance box; $R_1 \cdots R_6$, resistors; G1, pulse generator; C, variable capacitors; U1, high-frequency filter; A1, wide-band amplifier; DA1–3, comparators; DS, digital oscilloscope; PT, timer; DT, delay circuit; EL, flash circuit.

length is too short to switch on a convection mechanism. The time dependence of the probe resistance is recorded. The moment of the abrupt disturbance of the contact continuity (for instance, due to spontaneous nucleation) is marked by a characteristic signal related to the sharp change of the rate of the

probe resistance growth. The recorded equivalent of the resistance change is the potential of the bridge disbalance. The device for processing the disbalance signal contains two parallel circuits. One of them selects the useful signal against the background of smooth heating and consists of a high-frequency filter U1 and a wide-band amplifier A1. The filter consists of the capacitance branch of the bridge ($C - C$) and coaxial transforming line with the electromagnetic coupling of type Z (1 : 16). To separate the useful signal most effectively, the filter parameters can be tuned within the range from 5 to 500 kHz.

The other circuit consists of a branch of the bridge R_1–R_b and a potential difference comparator DA1 and serves for determination of the probe resistance r (and temperature) at a time of interest. At a zero bridge unbalance, the comparator generates a mark in the form of a potential step. Using a resistance box R_b, the moment of the bridge balance can be brought into coincidence with the onset of the response signal. A typical oscilloscope trace is shown in Figure 3. From the balancing condition of the bridge, using the temperature dependence of platinum resistance, the temperature of the probe averaged over the bulk $\langle T \rangle$ is determined. Corrections[2,3] for the end and radial effects are introduced to determine the surface temperature in the middle part of the probe that is taken for T^* of a
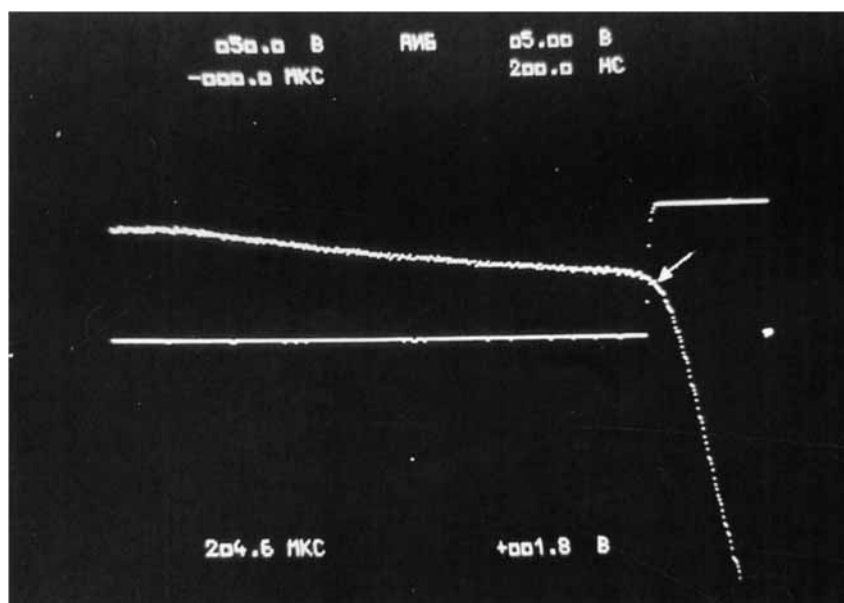
Figure 3 A typical oscillogram of T^* measurement. The upper beam is a signal from the probe. The arrow shows the beginning of a characteristic response against the background of smooth heating. The lower beam is a signal from the comparator. A step indicates the balance of the bridge.
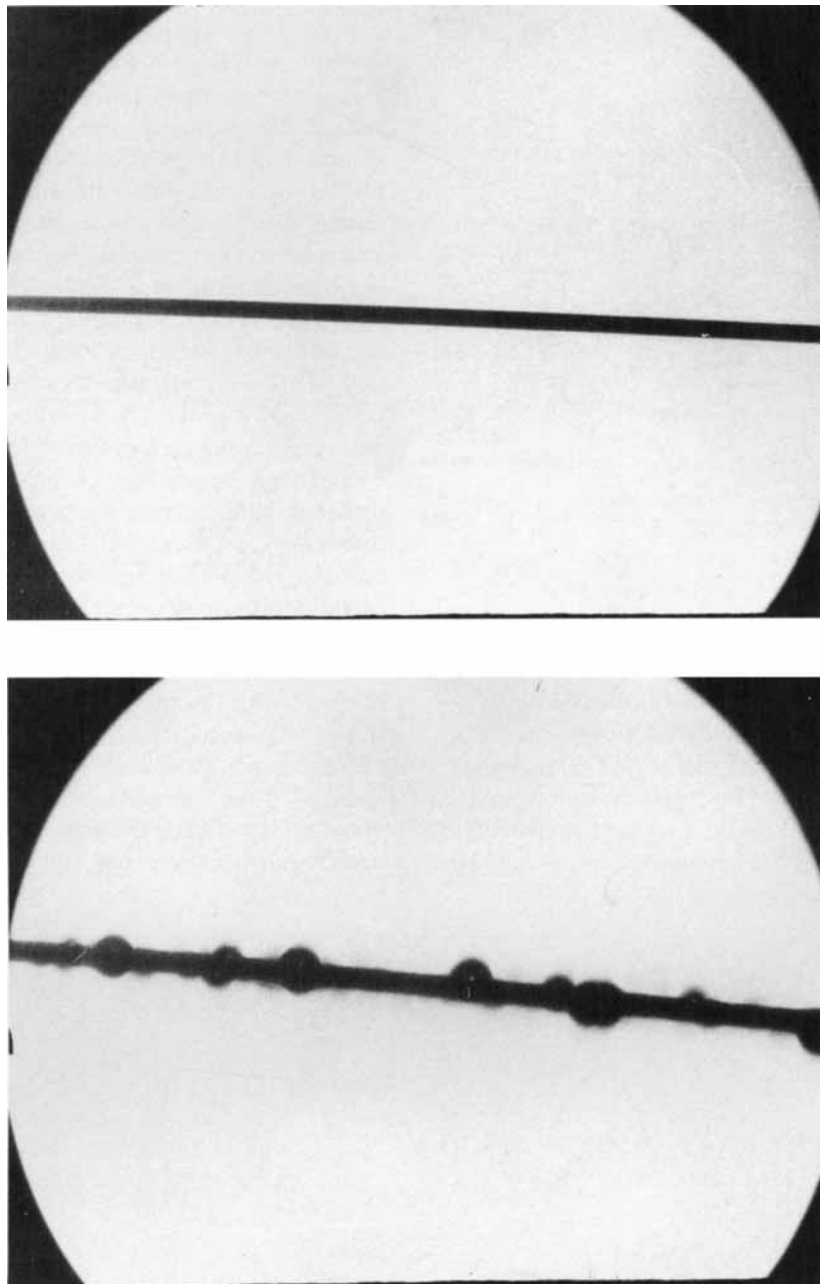
Figure 4   Photographs of the probe, placed in MMA (a, b, c) and ODMS $\bar{M}_n = 5.5 \cdot 10^4$ (d, e, f) at different stages of the response formation. $\tau_f - \tau_*$: (a) -5 μs; (b) 1 μs; (c) 3 μs; (d) -5 μs; (e) 3 μs; (f) 1.5 s. Here, τ_f is the flash moment, and τ_*, the moment of the response signal appearance. $T^* = 497$ K (MMA) and 955 K (ODMS).

substance. For the values of d, l, and τ used, the total correction is not large, being of the order of $(0.5\text{–}3.5)$ % $\langle T \rangle$.

The error of T^* determination is estimated to be 1%. It includes the instrumental error and the inaccuracy of the corrections. The instrumental error due to the error in the determination of r and the

delay time of the comparator was determined in special experiments. No delay has been found in the transmission of the signal front with the unit U1 for the oscilloscope sweep time of 100 ns per point. For applications, it is more important to know the change in T^* at a definite change of the properties of a system than the absolute value of T^*. In this
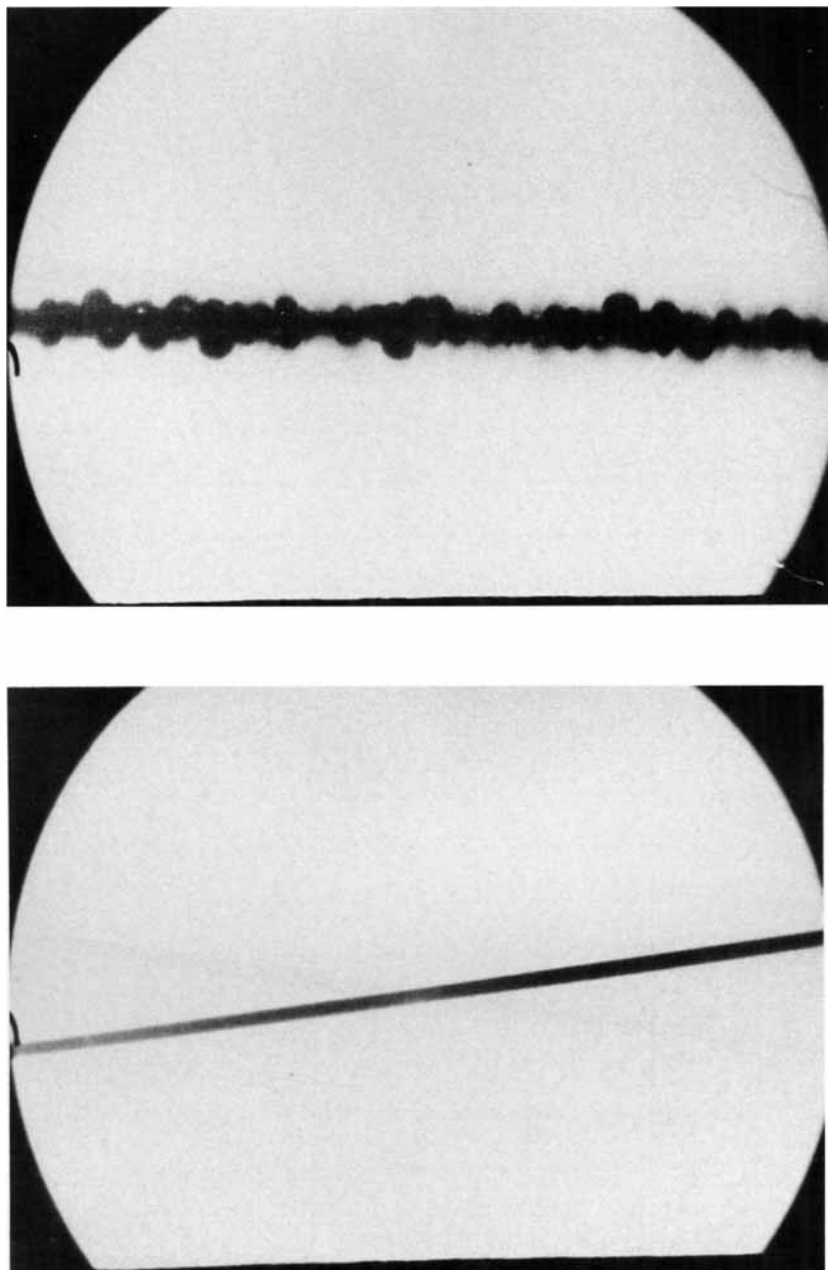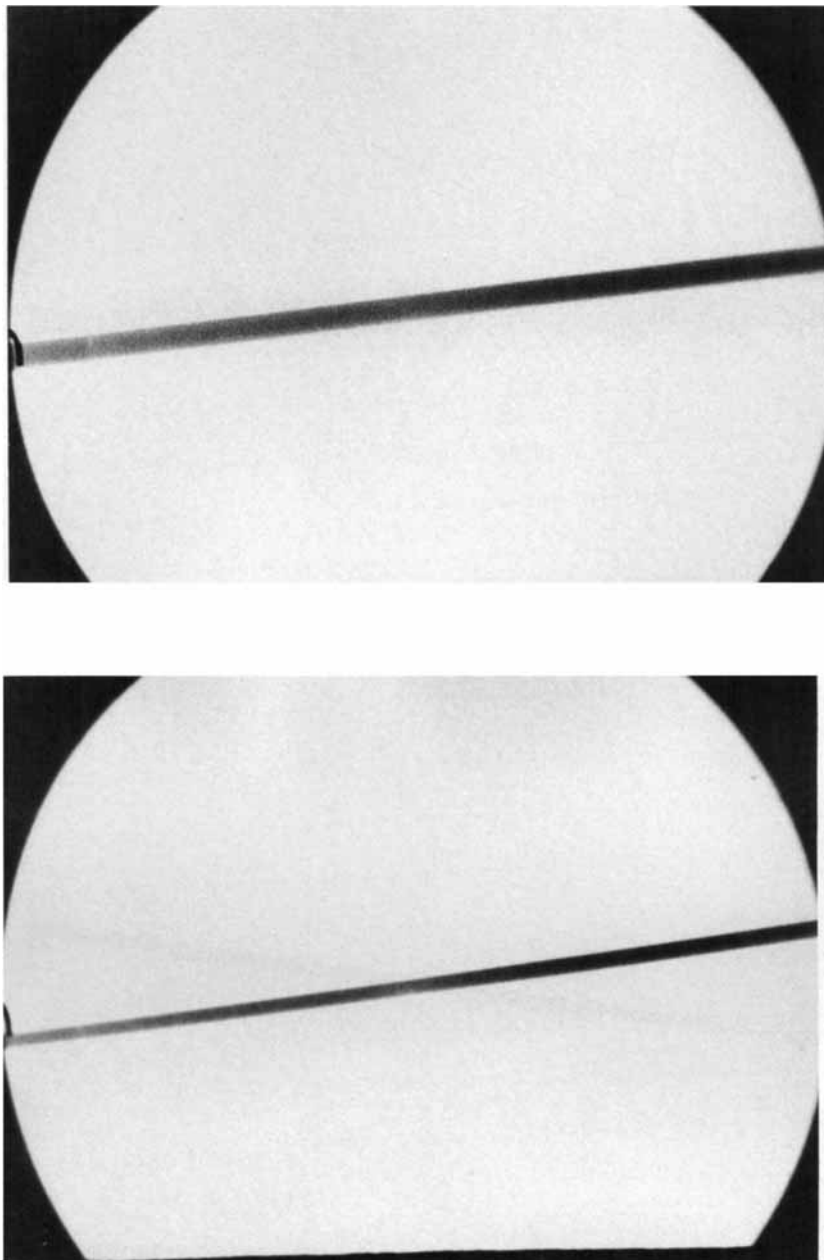
Figure 4 (*Continued from the previous page*)

case, the error due to the correction is essentially compensated.

A system of visual control, which consists of a flash with a light pulse length of ≤ 0.5 μs, a delay circuit, and a microscope, makes it possible to compare any point of the oscilloscope trace with the pattern of the process on the probe. Photographs of the probe at different stages of the response formation are given in Figure 4. For low molecular weight liquids, the onset of a response signal coin-

cides with the appearance of hemispherical bubbles.[2,3] In the case of high molecular weight liquids, the response corresponds to the apparent thickening of the probe. This fact can be explained by the formation of a continuous vapor film around the probe. Usually, the heating pulse is turned off at the earlier stage of boiling by a device tuned to a relatively small amplitude of the response signal. The relaxation time of the surface layer t_r after heating to T^* was about 1 s for both substances.

Figure 4 (*Continued from the previous page*)

The analysis of a number of factors affecting the stability of T^* measurements has shown that for our purposes the optimal value of the heating pulse length τ_* is in the range from 50 to 100 μs. The pulse repetition rate f is determined by the time t_r being evaluated experimentally. The results of f measurements for an oligodienurethanepoxy with a steep temperature dependence of viscosity are shown in Figure 5. The chosen f_m value corresponded to the maximum repetition rate at which one still could not observe a systematic drift of T^* values typical of the process of accumulation of evaporation or thermodecomposition products.

Method of Time Interval Measurements

The average rate of the temperature increase is recorded for a probe heated by relatively weak potential pulse with a highly stable amplitude. The time interval $\Delta\tau$ between the moments at which the probe

$1/f_m$ (s)

$\ell g\ \eta$ (Pa·s)
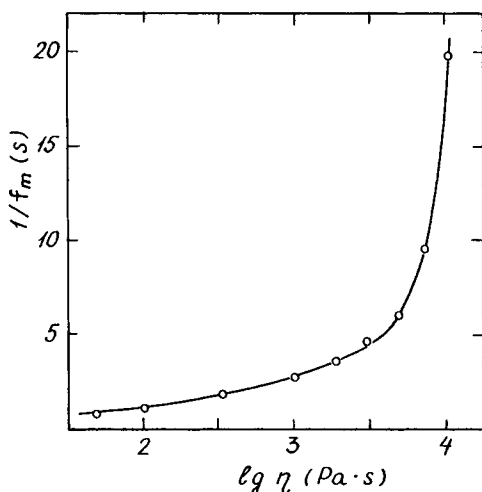
Figure 5 Pulse repetition rate vs. viscosity of oligo-dienurethanepoxy.

temperature reaches given values T_1 and T_2 is measured in the experiment. Since the values of $\Delta\tau$ depend on the probe length l, measurements using this method are relative. The probe heating rate $\dot{T}(\tau)$ at a given volume heat release in the probe $q(\tau)$ is determined by the heat flow into a substance $q'(\tau)$. The solution of the heat-conduction equation applied to the conditions of our experiments with the approximations $\dot{T} = const$ and $l = \infty$ gives the proportionality between the quantities q' and b. Indeed, experiments determining $\Delta\tau$ for a number of liquids with different relations of thermal parameters (λ, ρc, a, b)[14] have shown that the variation of $\Delta\tau$ is correlated with the variation of thermal activity.

The block diagram of the apparatus is shown in the right-hand part of Figure 2. The values of T_1 and T_2 are set by variable resistors R_3 and R_4. The time reading is started and stopped by signals from comparators DA2 and DA3 marking the balance of the corresponding bridge branches. The heating pulse length is 500 μs and the difference $T_2 - T_1$ is chosen in the range from 10 to 100 K. The scatter of $\Delta\tau$ values due to deviations of the pulse parameters and the delay time of comparators is about 0.25 μs. This corresponds to the sensitivity of the apparatus to changes in the b values of the order of 0.5 J s$^{-0.5}$ m^{-2} K^{-1}.

The method is used to monitor the relaxation time t_r. For this purpose, measurements of $\Delta\tau$ are carried out just before ($\Delta\tau_1$) and after ($\Delta\tau_2$) the heating pulse (T^*). If on the surface of the probe there remain bubbles, unwetted areas, or products of thermodecomposition, the values of $\Delta\tau_1$ and $\Delta\tau_2$ do not coincide. In experiments on reacting systems, we

determined first the background curve $\Delta\tau(t)$, where t is the current time of the reaction. This curve showed the scale of changes in $\Delta\tau$ during the time interval between two pulses. Besides, the knowledge of trends of the thermal activity variation for a reacting system proves to be useful in analyzing the reaction kinetics.

Measurements

Measurements of temperature T^* and time interval $\Delta\tau$ have been carried out in melts of poly(ethylene oxides) (PEO) of different molecular weight M and their binary solutions. The investigated range of M was from a monomer to lg $(M) \simeq 6.3$ and the range of polydispersity D of the solutions was from 1.1 to 6.5. The pressure varied from 10^{-3} to 4 MPa. Similar measurements were performed in the process of polymerization of methyl metacrylate (MMA) using benzoyl peroxide as an initiator (2 wt %) and in the processes of curing of macro(diisocyanate) with diamine (13 wt %) and the epoxy oligomer ED-20 with triethanolamine titanate (TEAT) (13 and 29 wt %). The reaction temperature in the first case was 343 K, in the second case from 343 to 363 K, and in the third case from 353 to 413 K. The pressure was ambient. Procedures of the reaction conducting were taken from Refs.[15-17] Solutions of carbon dioxide in oligopropylene oxides (OPO) with $\bar{M}_n$ from 400 to 5000 and in oligodimethylsiloxanes (ODMS) with $\bar{M}_w \simeq 2\cdot10^4$ and $5.5\cdot10^4$ were also studied. The range of concentrations C was about 0–30 wt %. The concentration of carbon dioxide was determined simultaneously by the gravimetric method. The pressure varied from the gas saturation value $p_r \simeq (0.1 \div 5)$ MPa to a certain limiting value p_l, at which the response signal (T^*) was no longer resolved.

Measurements were carried out in a thermostabilized pressure chamber with a removable cell for the substance under investigation. The schematic diagram of the chamber with the systems for evacuation and gas saturation is shown in Figure 6. In most cases, the cell was a thin-wall glass vessel with a volume of 1 cm^3, shown in Figure 6. The pressure was created by a gas with a low solubility, helium, or hydrostatically. In the latter case, the cell was a Teflon vessel cut off from the gas line. The pressure was created with a piston. The walls of the vessel served as an elastic element transmitting pressure. The wall thickness was 0.1 mm. The pressure drop at the walls did not exceed 0.03 MPa. The design of the cell for studies of T^* (p) dependence for gas-saturated oligomers was somewhat more compli-
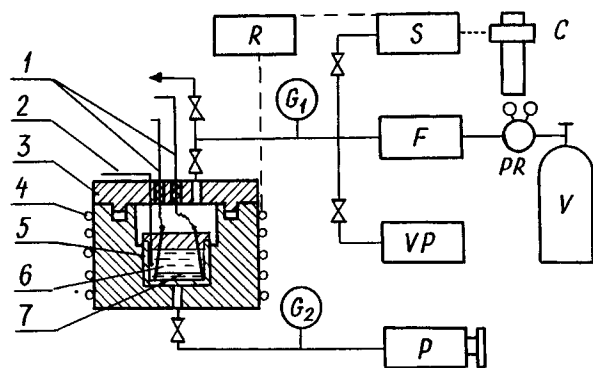
Figure 6 Schematic of side view of the pressure chamber with systems of evacuation and gas saturation: (1) lead-in wires; (2) thermocouple; (3) thermostabilized pressure chamber; (4) nichrome heater; (5) glass vessel; (6) substance under investigation; (7) probe; (R) thermostatic regulator; (S) hermetical scales; (C) cathetometer; (F) water-absorbing filter; (G_1, G_2) pressure gauges; (VP) vacuum pump; (PR) pressure regulator; (V) vessel with CO_2 or He; (P) piston.

cated.[18] It was made of stainless steel and had a peephole for a visual control of the liquid level and a movable bottom that served to account for the effect of swelling, to push out the gas phase after the saturation, and to create the pressure in the solution. To measure T^* values for the solution at different pressures, the vapor phase was pushed out of the cell and the cell was cut off from the gas line. The pressure was transmitted by means of a rod. The pressure drop at the rod seals was 0.2 MPa. The coincidence of T^* (p) curves obtained with increasing and decreasing pressure indicated that the properties of a solution were unchanged during the experiment.

A device operating on the principle of "scales-fishing-rod" was used to evaluate the solubility of carbon dioxide in the polymers. The mean-square error of measurements was 5%. The results on the solubility of carbon dioxide in n-eicosane are consistent with the known data[19] for this system.

Materials

To investigate the possibilities of the application of the pulse thermal probe technique to monitor polymer systems' parameter changes, we used a wide range of materials. A homologous series of PEO was obtained from "Merck-Shuchardt." The other chemicals were commercial grade, produced in Russia. Polystyrene was fractionated in the usual way,[20] $\bar{M}_w = 164 \cdot 10^3$, determined by the light-scattering method. For preparing solutions with CO_2, we used

oligodimethylsiloxane (ODMS) $(\bar{M}_w = 55 \cdot 10^3$, gel permeation chromatography) and difunctional oligopropylene oxides (OPO) $(\bar{M}_w = 400; 600; 1.6 \cdot 10^3; 2.1 \cdot 10^3; 5 \cdot 10^3)$, which are the initial oligomers for elastic urethane foams production. CO_2 was purified of water. The content of impurities was 0.8 vol % of N_2 and 0.2 vol % of O_2.

The procedures of reactive sample preparation were taken from Refs. 15–17. MMA had the following characteristics: $d_4^{20} = 0.943$, $n_D^{20} = 1.4145$, and bp = 100°C. Macro(diisocyanate) was synthesized from poly(tetramethylene glycol) and 2,4-toluene diisocyanate, respectively, in the ratio 2 : 1. The content of NCO groups was 6.5%. 3,3-Dichlo-4,4-diamine diphenylmethane (mp = 103.2°C) was used as a current agent. This polymer is essentially analogous to the well-known Adipren L-167 (DuPont, USA). Epoxy oligomer ED-20 $(\bar{M}_n = 400$, ebullioscopic method) contained 21% of epoxy groups, equivalent weight per epoxy group (EE) was 204.7, $d_4^{20} = 1.162$, and $n_D^{20} = 1.5739$. Triethanolamine titanate (TEAT) $(\bar{M}_n = 366)$ contained 4.7% of butoxy groups; the equivalent weight per hydroxyl group (HE) was 170, $d_4^{20} = 1.330$, and $n_D^{20} = 1.5537$.

Before measurements, the oligomers were evacuated at an elevated temperature. The removal of volatile impurities was monitored by repeated T^* measurements. In this case, the value of T^* showed the monotonic growth, and the derivative $\partial T^*/\partial t$ decreased until T^* reached a stable value, which was taken for the temperature T^* at $p = 10$ kPa. For instance, the sensitivity of the method to the content of water in PEO was $(2-3) \cdot 10^{-2}$ wt %. Solutions of CO_2 in an oligomer were prepared by saturating liquid through a free surface. The saturation kinetics was monitored by repeated T^* measurements. The termination of changes in T^* with respect to current time and the height of the liquid column indicated the establishment of the equilibrium composition at fixed p and T.

RESULTS AND DISCUSSION

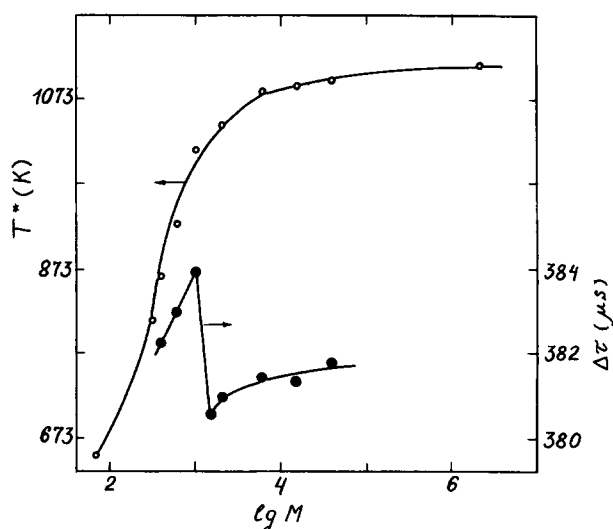### Molecular Weight and Polydispersity

The sensitivity of the method to changes in the chain length and the degree of its heterogeneity is an important criterion of the efficiency of the method of monitoring the state of a polymeric or polymerizing system. For this reason, measurements have been made on both polymer homologs PEO and their binary mixtures. The choice of PEO as a basic system is caused by its narrow molecular weight distribu-
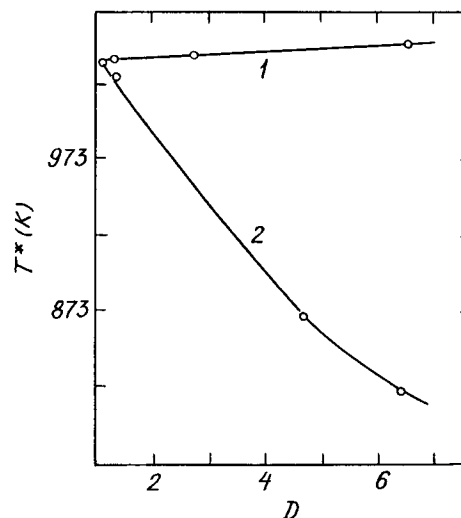
tion. The main results are given in Figures 7 and 8. The dependencies of $T^*(M)$ and $T^*(\dot{T})$ have the shape that is typical for the corresponding dependencies of the temperature of a phase or relaxation transition in a polymer. The stabilization of properties determining the response temperature is indicated by the natural tendency of T^* to level off. The kinetics of accumulation and the degree of fragmentation of thermal decomposition products, the surface tension, and the vapor pressure at $T = T^*$ are of special importance. The external pressure increases the value of T^* (several degrees per atmosphere) without perturbing the characteristic shape of the curve.

Measurements of $\Delta\tau$ have revealed the nonmonotonic change of the thermal activity with increasing M (see Fig. 7). This result is not unexpected, if one takes into account the correlation between the values of thermal properties and the density of molecular packing.[21] The character of the curve $\Delta\tau(M)$ coincides with that of the change of the macroscopic density $\rho(M)$ of PEO melts. In particular, both the dependencies have a minimum at $M \simeq 1.5 \cdot 10^3$. A sharp decrease in ρ at $M \simeq 1.5 \cdot 10^3$ is due to the intramolecular stretch-to-coil transition.[22] The decrease in $\Delta\tau$ in the vicinity of the same M value may be considered as a qualitative confirmation of this hypothesis.

Since the dependence $T^*(M)$ is nonlinear, one can obtain information on the degree of polydispersity of a system. Measurements have been performed on binary PEO solutions with different $D = \bar{M}_w / \bar{M}_n$ at a fixed value of the number-average molecular


Figure 8 Response temperature of binary PEO solutions vs. polydispersity. $\bar{M}_n = 2 \cdot 10^3$, curve 1; $\bar{M}_w = 2 \cdot 10^3$, curve 2.

weight $\bar{M}_n$ (Fig. 8, curve 1) or the weight-average molecular weight $\bar{M}_w$ (curve 2). The data presented in Figure 8 show that the value of T^* of a polydispersed system is more sensitive to the presence of low molecular polymer homologs. The method of T^* measurements may be also used to evaluate the $\bar{M}_n$ of molten polymers.

Polymerization and Curing

The sensitivity of the temperature T^* to the molecular weight of polymer homologs and to the content of a low molecular weight component implies the possibility of a considerable change of T^* in the process of transformation of a monomer or oligomer into a polymer. The results of measurements carried out on a number of reacting systems with different kinetic mechanisms are given in Figures 9-11. The smooth curves are drawn through the experimental points. For all the studied systems, a monotonic increase of both T^* and $\Delta\tau$ during the reaction is observed. This fact provides a certain basis for monitoring the process kinetics by measuring these parameters. The analysis of the experimental data obtained at different reaction temperatures and different reagent ratios allows one to make the following qualitative conclusions. The rate of $T^*(t)$ and $\Delta\tau(t)$ growth and the scale of their change are correlated with the rate of conversion change $\dot{\Phi}(t)$ and the limiting value $\Phi(t)$ for the reaction conditions. The level of T^* values is determined mainly by the nature and the content of a relatively low molecular weight component. The character of $\Delta\tau$ changes re-
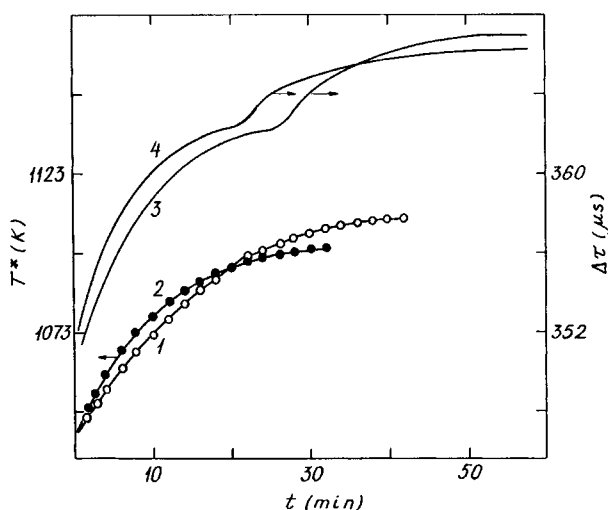

Figure 7 Response temperature and time interval vs. molecular weight of PEO. $\tau_* = 50 \ \mu s; p = 0.6$ MPa.
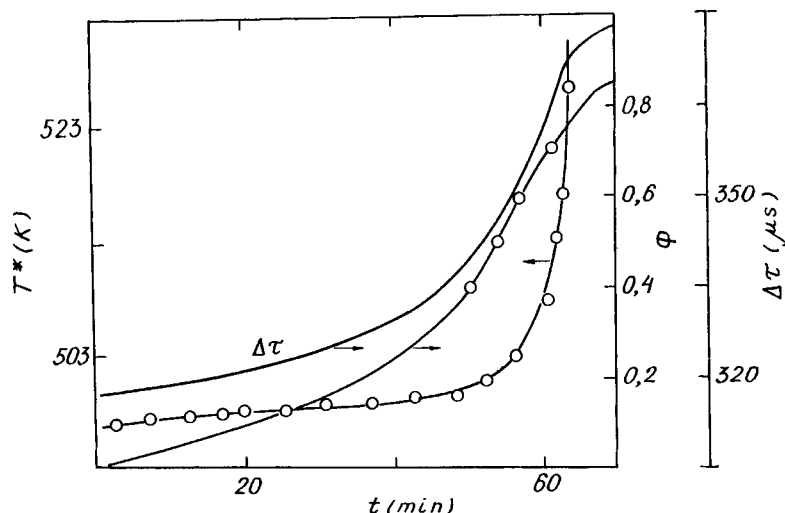
Figure 9 Response temperature, time interval, and degree of conversion of MMA vs. polymerization time.

flects the trends in the change of the packing density and the degree of order of molecular structures.

The character of changes in T^* and $\Delta\tau$ in the process of MMA polymerization (see Fig. 9) is consistent with the concept of the essential nonadditivity of the dependence of T^* for a polymeric system on the solvent concentration[8,9] and also with the changes of thermal properties in a homologous series of PMMA.[23]

The system under investigation is a solution of stable macromolecules in its own monomer. In the case of block polymerization, the mass fraction of a polymer in a reacting system is equal to the degree

of conversion of a monomer. This allows one to evaluate the current values of Φ from T^* measurements. For this purpose, we have performed T^* measurements for the solutions of PMMA in a monomer with the PMMA content up to 70 wt % under stationary conditions. By comparing these results with the data on $T^*(t)$, we find the approximation for the kinetic curve $\Phi(t)$. Its shape is typical of the process of block MMA polymerization. As the viscosity of the system increases, the ampli-

Figure 10 Response temperature and time interval of macro(diisocyanate)-diamine system vs. curing time. T_0: 343 K (curves 1 and 3); 363 K (curves 2 and 4).
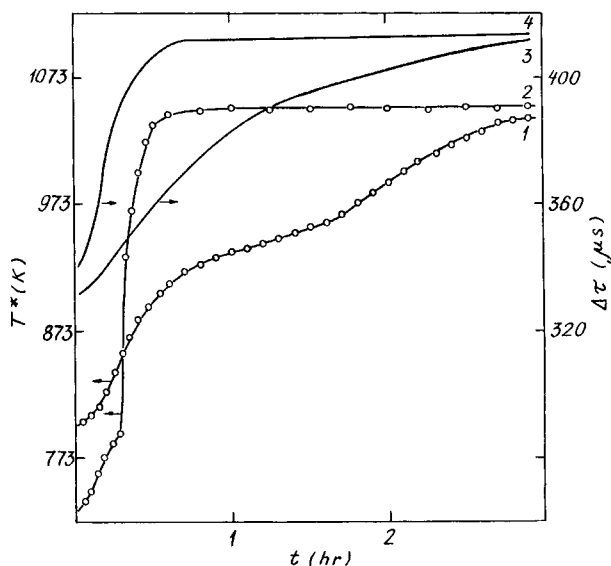
Figure 11 Response temperature and time interval of an epoxy oligomer–TEAT system vs. curing time. $T_0 = 393$ K; TEAT content: 13 wt % (curves 1 and 3) and 29 wt % (curves 2 and 4).

tude of the response signal shows the monotonic decrease, and at a certain level of Φ, it becomes unresolvable. Thus, the stiffness of the system sets practical limitations on the applicability range of the method of T^* measurements. These limitations do not apply to the method of $\Delta\tau$ measurements.

For curing of reactive oligomers, the level of temperatures T^* is much higher than in the above-discussed case. Figure 10 presents the results of measurements carried out in the curing process of a segmented polyurethane. The main increment in T^* and $\Delta\tau$ is observed at the first stage of the reaction proceeding by the mechanism of linear polycondensation up to the formation of a visually insoluble fraction. The progressive slowing down of the reaction after the gel point has an effect on the rate of changes in T^* and $\Delta\tau$ as well. The increase in $\Delta\tau$ is evidently related to the onset of molecular-ordering regions (the first stage of the reaction) and to the increase in the real component G' of the dynamic modulus[16] in the second stage. The essential rise in $\partial(\Delta\tau)/\partial t$ at the second stage can be explained by phase separation of aggregating segments in the network polymer accompanied by the decrease in the imaginary component of dynamic modulus.[16] The character of the increase in T^* prior to the gel point is consistent with the shape of the $T^*(M)$ dependence. The maintenance of the response signal in a viscoelastic state may be explained by the presence in the system of a certain quantity of relatively low molecular weight products. The amplitude of the response shows the monotonic decrease, and on achieving a certain value of G', it is no longer resolved.

The largest range of variations of T^* and $\Delta\tau$, i.e., the greatest difference between the thermal properties of the initial and the final product, has been revealed in the process of the epoxy oligomer–crosslinked polymer transformation (see Fig. 11). This is due to a number of favorable factors: a relatively low level of the temperatures T^* of reagents, 820 and 655 K, respectively, and the maintenance of the response signal, as in the case of curing of elastomers,[11] up to the completion of the reaction. Measurements have been carried out for two ratios of reagents: With the excess of epoxy oligomer ($EE/HE = 4.5$) and with the ratio of epoxy and hydroxyl groups close to the equivalent one ($EE/HE = 1.2$). The increase in $\Delta\tau$ reflects the growth of molecular-ordering regions and the increase in the degree of the network development. The increase in T^* in the melt media is explained by the growth of the chain length as a result of interaction between epoxy groups and hydroxyl groups of TEAT. The steepest
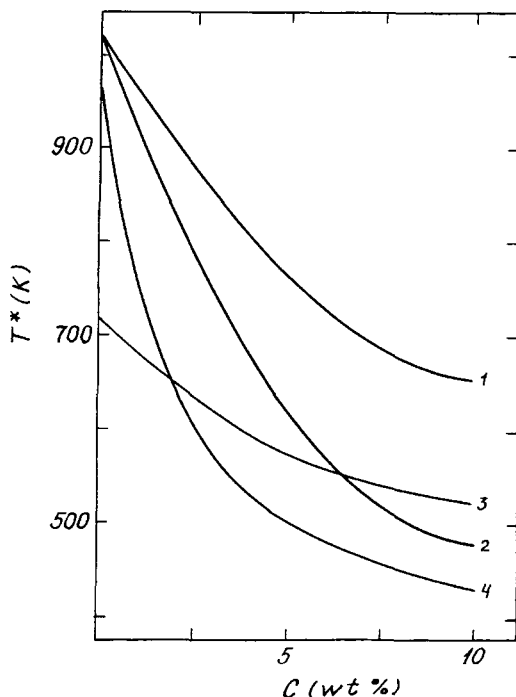
section of the curve corresponds to the transition of a system into a high-elasticity state. In this case, there are characteristic changes in the parameters of the response signal.[9] Its origin is probably related to the confined-in-time formation of rarefied zones in the substance layer adjoining the probe. Evaluations have shown that the probe temperature perturbation (or the response signal amplitude), connected with a sharp decrease of heat removal at $T = T^*$, is equivalent to the appearance of nonthermoconducting microvoids that occupy 2% of the area of the probe surface. With growing cross-linking, the temperature T^* shows the monotonic increase. When the reaction is complete, a polymeric system can stand up to 100 heating pulses with reproducible values of T^*, i.e., without any irreversible destruction of the boundary layer, at $f_m = 0.5$ Hz.

Solubility of Gases in Polymeric Liquids

The high sensitivity of the temperature T^* to the presence of a low molecular weight substance is most fully revealed in studies of gas solutions in polymers. Such systems have been intensively studied over the past few years. A gas that is present in a polymeric solution affects the technological process as well as the structure of solids formed thereof.[24] The results of $T^*(p)$ measurements on CO_2 solutions in OPO are shown in Figure 12. With the dissolution of CO_2,
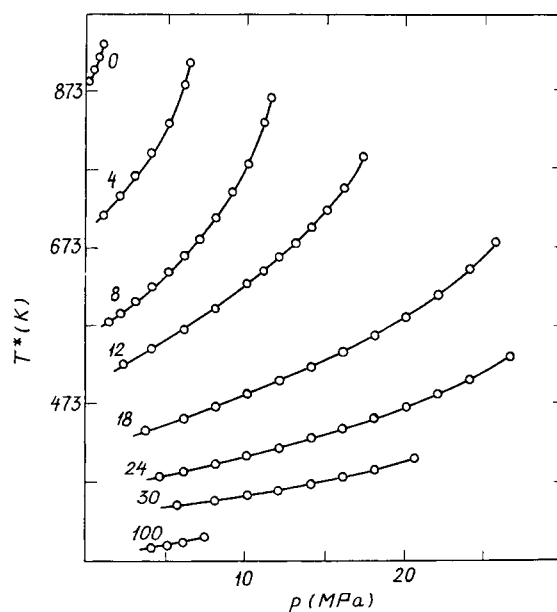
Figure 12 Response temperature for CO_2 solutions in OPO $\bar{M}_n = 1600$ vs. pressure. Indicated numbers are the CO_2 content (wt %).

erties of the system is compared to changes in the characteristic temperature of the response (superheat) and in the thermal activity. In particular, the method allows one to evaluate the number-average molecular weight and the concentration of a dissolved low molecular weight component, e.g., gas, and to trace the kinetics of its dissolution or removal and the kinetics of polymerization and curing, and to detect conformational changes in a polymer melt. While discussing the results of experiments, it is necessary to take into account that the behavior of the thermal activity of polymeric systems has been studied poorly. The information on high-temperature short-living states of polymers is lacking. The values of T^* and $\Delta\tau$ measured in the experiment depend on a number of factors manifesting themselves on the structural micro- and macrolevel and resulting in the integral effect of their interaction. Therefore, the interpretation of our results is not conclusive. Besides the test of the method, the present work gives important information on the peculiarities of the response of polymers to pulse heating and on the trends in the change of thermal activity in polymeric system.

Figure 13 Response temperature vs. low molecular weight component content for the systems: OPO ($\bar{M}_n$ = 5000)–water (curve 1) and CO_2 (2); hexadecane–CO_2 (3); ODMS–CO_2 (4); p = 1 MPa.

the value of T^* decreases more steeply than by the additive law. With increasing concentration, the slope of the $T^*(C)$ dependence decreases. The limiting pressure for the resolution of the response signal in the solution increases and may exceed the values of p_l for pure components by an order of magnitude. The qualitative form of the dependencies $T^*(C)$ and $p_l(C)$ is common for all the investigated gas–polymer systems. This fact indicates that the method can be used to monitor the kinetics of gas dissolution in oligomers by observing changes in T^* and/or p_l. For small concentrations of CO_2, the resolution of the method in our experiments was from 0.1 wt % (hexadecane) to 0.01% (ODMS) for T^* measurements (see Fig. 13) and of the order of 0.1% for p_l measurements. The sensitivity of $\Delta\tau$ values to the addition of gas component appeared to be an order of magnitude lower.

CONCLUSIONS

The applicability of the method of the pulse thermal probe for monitoring the processes in polymeric systems has been shown. The change of the prop-

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