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STUDY OF THE POLYMERIZATION OF SOME METHACRYLIC ACID ESTERS BY DIFFERENTIAL SCANNING CALORIMETRY

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The strengths of the gel effect, and the monomer conversions at which the gel effect sets in for the polymerizations of some methacrylic acid esters, were determined at different temperatures from the courses of polymerization measured by differential scanning calorimetry. It was found that the strength of the gel effect is greatly influenced by the reaction temperature and the ester residue in the molecule of the monomer, whereas the "critical" conversion for individual monomers is practically independent of the reaction temperature in the measured interval, but is strongly dependent on the length of the ester residue.

The isothermal radical polymerization of methacrylic acid esters, and especially of methyl methacrylate (MMA), have been studied by many authors. It is known that the classical free radical kinetics are valid only at low conversions. As the reaction proceeds, the concentration of the macromolecules and the viscosity of the reaction mixture increase. The chain termination rates are therefore diminished and the gel effect sets in [1]. There are some kinetic models describing the polymerization of MMA at high conversions [2–7]; these also try to establish the conversion at which the gel effect starts. In these works the already published data obtained by "classical" dilatometry were used for calculations [8]. In the oresent work differential scanning calorimetry was used to measure the course of the isothermal polymerization over the entire range of conversion and to determine the onset of the gel effect.

Experimental

The radical polymerization of some methacrylic monomers was investigated isothermally at different temperatures with a Perkin–Elmer DSC-2 differential scanning calorimeter. As initiator, 2,2′-azoisobutyronitrile (AIBN) was used. The reaction mixtures were put into the calorimeter, which was set at the selected temperatures.

From the DSC curves, the course of the polymerization was followed. Conversions at different reaction times were calculated from the area between the DSC curve and the baseline, which was obtained by back-extrapolation of the straight line, recorded after the polymerization was finished.

The calorimeter was calibrated with reference to the melting heat of indium. The DSC curves were digitalized on-line and processed by computer.

Monomers were freed from inhibitor and distilled under nitrogen at reduced pressure. The initiator was recrystallized from absolute ethanol.

Results and discussion

The isothermal polymerizations of MMA, ethyl methacrylate (EMA), butyl methacrylate (BMA), and isobutyl methacrylate (IBMA) were studied at 353, 358, 363 and 368 K with the addition of 5×10^{-2} mol/l AIBN. Figure 1 shows the courses of tion of EMA at different temperatures. The courses for all the studied methacrylates are similar, i.e. the gel effect sets in after the steady-state reaction in the early stage.

From the diagrams it can be seen that the gel effect is the most expressed in the polymerization of MMA, and the least in the polymerization of BMA. It can be polymerization of MMA, and the least so in the polymerization of BMA. It can be concluded that the intensity of the gel effect depends on the length of the ester residue in the molecule of the methacrylic acid ester. These findings do not agree in full with the theories, which were based on measurements of the polymerization of MMA only, and describe the gel effect as a result of the reduced termination rate constant due to the increasing viscosity of the reaction mixture and the limited diffusion, respectively [2–5].

In the published models the onset of the gel effect is defined in different ways. From the DSC curves in Fig. 1, the simple conclusion can be drawn that the onset of the gel effect coincides with the sharp release of the reaction enthalpy. Analysis of the DSC curves reveals that the conversions at the onset of the gel effect for the individual monomers are practically independent of the reaction temperature, but strongly dependent on the length of the ester residue in the molecules of the methacrylic acid esters: the shorter the ester residue, the lower the conversion at onset of the gel effect. It was found that the gel effect for the polymerization of MMA starts between 41 and 43% conversion, and most probably at 42.5%, which is the average of several measurements. The values for the other monomers are given in Table 1. The "critical" conversion was obtained by graphical extrapolation. The values for the individual measurements display a scatter of approx. ±1% conversion. Two other phases of the polymerization, which can also be considered as the onset of the gel effect, can easily be obtained from the DSC curves. These are the deviation from linearity in the diagram for the first-order reaction with respect to monomer concentration [9] and the deviation from linearity in the conversion *vs.* time diagram. The values are given in Table 1.

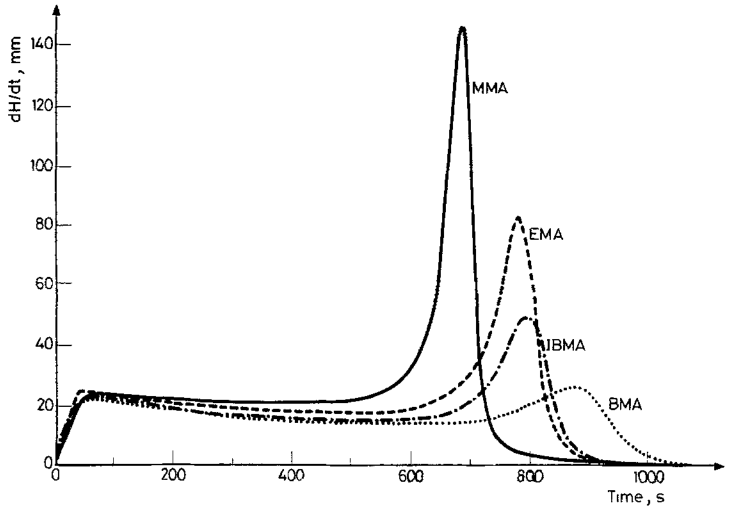

Fig. 1 Courses of polymerization of MMA, EMA, IBMA and BMA. $T = 363$ K, [AIBN] = $= 5 \cdot 10^{-3}$ mol/l

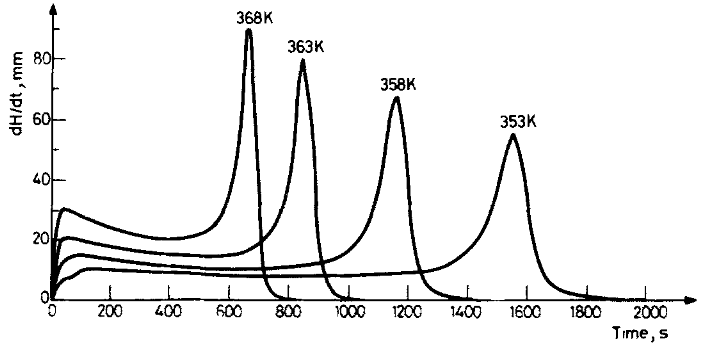

Fig. 2 Courses of polymerization of EMA at different temperatures

Table 1 Conversions at the onset of the gel effect for some methacrylic acid esters

Monomer	Conversion, %		
	Onset of the sharp increase in release of ΔH	End of linearity in 1. order diagram	End of linearity in the diagram conversion-time
MMA	41 – 43	24 – 26	42 – 44
EMA	51.5 – 53.5	32 – 34	52 – 54
IBMA	57.5 – 59.5	38.5 – 41	60 – 62
BMA	67 – 69	38.5 – 40.5	68.5 – 70.5

From Table 1 it can be seen that the values of the first and third columns are very similar.

Conclusions

It was found that the strength of the gel effect and the monomer conversion at which the gel effect sets in are strongly influenced by the length of the ester residues in the molecules of the methacrylic acid esters. These findings do not agree completely with the proposed theories for accelerated polymerization.

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Zusammenfassung — Die Stärke des Geleffektes und die Monomerkonversion, bei der der Geleffekt bei der Polymerisation einiger Methacrylsäureester einsetzt, werden aus dem Verlauf der Polymerisation in Abhängigkeit von der Temperatur mittels DSC gemessen. Es wurde festgestellt, daß die Stärke des Geleffekts stark von der Temperatur und dem Esterrest im Molekül des Monomeren beeinflüßt wird, während die "kritische" Konversion individueller Monomere praktisch unabhängig von der Temperatur im untersuchten Bereich ist, jedoch im starken Maße von der Länge des Esterrestes abhängt.

Резюме — Сила гель-эффекта и превращения мономера, при которых гель-эффект вызывает полимеризацию некоторых сложных эфиров метакриловой кислоты, были определены при различных температурах. исходя из процесса полимеризации, изученного с помощью метода дифференциальной сканирующей калориметрии. Найдено, что сила гель-эффекта в значительной степени зависит от температуры реакции и эфирного остатка в молекуле мономера, тогда как "критическое" превращение отдельных мономеров практически не зависит от температуры реакции в измеренном интервале температур, но сильно зависит от длины эфирного остатка.