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POLYMERIZATION OF METHYL METHACRYLATE AND ETHYL METHACRYLATE IN DIFFERENT SOLVENTS STUDIED BY DSC

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ABSTRACT

The courses of polymerization of 80 wt. % solutions of methyl methacrylate (MMA) in n-hexane (H), cyclohexane (CH), toluene (T), n-butyl acetate (BA), cyclohexanone (CON), dioxane (D), N-methyl pyrrolidone (MP), dimethylformamide (DMF), and isobutyl alcohol (IBA) as the courses of polymerization of 80 wt. % solutions of ethyl methacrylate (EMA) in dioxane (D), N-methyl pyrrolidone (MP), and isobutyl alcohol (IBA) at 358 K in the presence of 5 mmol/L of 2,2'-azoisobutyronitrile (AIBN) were measured in a differential scanning calorimeter DSC-2, Perkin Elmer.

From the DSC curves the enthalpies of polymerization and the composite rate constants for the initial steady state polymerization were calculated.

It was found that the maximal reaction rate in the region of the gel effect and the composite rate constants are influenced by the solubility parameter of the solvent, i.e. the constants increase with the increasing value of the solubility parameter.

INTRODUCTION

The radical polymerization of vinyl monomers is influenced by the presence of a solvent (1,2). Particularly the effect of aromatic solvents on the polymerization of MMA was studied by many investigators (3-7). The variation of the propagation rate constants in different solvents was explained as a result of formation of a complex between the propagating radical and the solvent. The influence of the solvent viscosity was studied, as well (1,8). The results are not fully consistent and besides, other properties of solvents should also be taken into account.

In our previous work the correlation between the composite rate constants for the polymerization of MMA and the solubility paramter of the solvent was found (9). Therefore a number of solvents within a large interval of solubility

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parameters was investigated. Beside MMA, EMA was used as monomer.

EXPERIMENTAL

Monomers were freed of inhibitor and distilled under nitrogen in vacuum. AIBN was recrystallized from absolute ethanol. Solvents were of p.a. grade and distilled before use. The courses of polymerization of 80 wt. % solutions of MMA in H, CH, T, BA, CON, D, MP, DMF, and IBA, and the courses of 80 wt. % solutions of EMA in D, MP, and IBA were measured isothermaly at 358 K in a differential scanning calorimeter DSC 2, Perkin Elmer. The polymerization was initiated with 50 mmol/L of AIBN. The relative reaction rates were measured as ordinate displacements in mm, while for polymerization enthalpies and for composite rate constants the areas between DSC curves and the baseline were considered. The DSC curves were digitized on line and computer processed.

RESULTS AND DISCUSSION

The courses of polymerization of MMA solutions in different solvents are shown in Fig. 1. It can be seen that the solvent influences the initial rate of polymerization, the rate of polymerization in the region of the gel effect and the onset time of the accelerated polymerization.

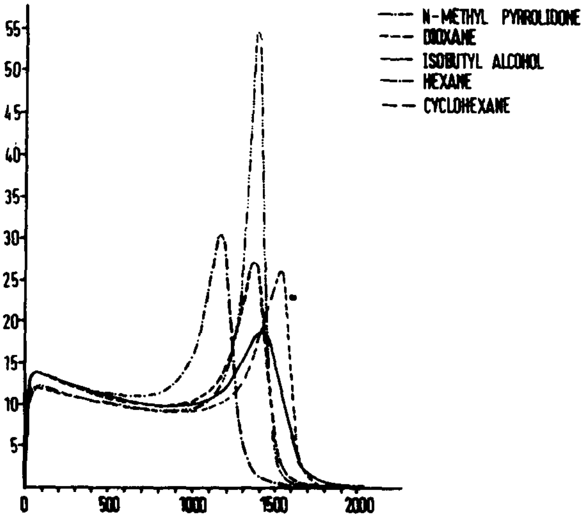

Fig.1.: Courses of polymerization of MMA in different solvents

The solution polymerization of EMA is shown in Fig. 2. For EMA, due to a smaller number of solvents with similar solubility parameter the differences are not so evident as for MMA.

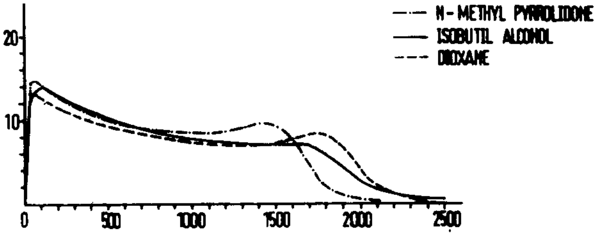

Fig.2.: Courses of polymerization of EMA in different solvents

The relative initial rates and the relative maximal rates in the gel effect region are given as ordinate displacement in Table 1, for MMA and in Table 2 for EMA.

In both Tables solvents were arranged in order of increasing solubility parameter values and hydrogen bonding parameters. H is a poorly hydrogen bonded solvent with the lowest solubility parameter, while IBA is a strong hydrogen bonded solvent with the highest solubility parameter. From Table 1 it can be seen that the quotient between the maximal and initial value of the MMA polymerization rate is the highest in H and the lowest in IBA. The low values of the quotients for T and BA are ascribed to close values of the solubility parameters between the two solvents and the monomer.

Similar decreasing of the quotient with increasing of the solubility parameter was observed for EMA solutions. However the maximal rates of the polymerization in the gel effect region are for the polymerization of EMA solutions lower than the initial rates. For IBA solution, the gel effect was even hard to detect.

Table 1: Relative initial rates and maximal rates in the gel effect region for polymerization of 80 % solutions of MMA in H, CH, T, BA, CON, D, MP, and IBA at 358 K

Solvent	Relative initial rate (mm)	Relative maximal rate (mm)	Quotient
Hexane	12.2	54.3	4.5
Cyclohexane	12.2	25.9	2.1
Toluene	11.5	15.7	1.4
Butylacetate	10.8	17.7	1.6
Cyclohexanone	12.5	25.1	2.0
Dioxane	13.4	27.2	2.0
N-methyl pyrrolidone	14.4	28.9	2.0
Dimethyl formamide	14.9	19.6	1.3
Iso-butyl alcohol	13.9	18.7	1.3

Table 2: Relative initial rates and maximal rates in the gel effect region for polymerization of 80 wt. % solutions of EMA in D, MP, and IBA at 358 K

Solvent	Relative initial rate (mm)	Relative maximal rate (mm)	Quotient
Dioxane	12.6	8.3	0.7
N-methyl pyrrolidone	14.5	9.6	0.7
Iso-butyl alcohol	14.3	7.3	0.5

The polymerization enthalpies for all experimental solutions were calculted from the areas between the DSC curves and the baseline. The values, extrapolated to 100 % monomer, are for MMA and EMA in the range 60.5 ± 1.5 kJ/mol.

Since the conversion is proportional to the polymerization enthalpy, from plots $\ln \frac{A}{A-a}$ *vs. time (where A is the total area and a is the partial area to time t) the composite first-order polymerization rate constants* k' *were calculated:*

k_d, k_p, and k_t are the rate constants for initiator dissociation, propagation and termination, and $|I_0|$ is the initial initiator concentration.

The calculated values are given in Table 3. The solvents in the Table are arranged again with regard to their solubility and hyrogen bonding parameters.

Table 3: Composite polymerization rate constants (k') in the polymerization of 80 wt. % solutions of MMA and EMA at 358 K in dependence on solubility parameter (δ) and hydrogen bonding parameter of the solvents (10)

Poorly hydrogen bonded			Moderately hydrogen bonded			Strongly hydrogen bonded		
MMA, $\delta = 18.0 \times 10^3$ $(J/m^3)^{1/2}$ (10), $k'_{bulk} = 0.67 \times 10^{-3} s^{-1}$ (11)								
Solv.	$\delta \times 10^{-3}$ $(J/m^3)^{1/2}$	$k' \times 10^3$ (s^{-1})	Solv	$\delta \times 10^{-3}$ $(J/m^3)^{1/2}$	$k' \times 10^3$ (s^{-1})	Solv.	$\delta \times 10^{-3}$ $(J/m^3)^{1/2}$	$k' \times 10^3$ (s^{-1})
H	14.9	0.62						
CH	16.7	0.65						
			BA	17.3	0.57			
T	18.2	0.67						
			CON	20.2	0.71			
			D	20.5	0.74			
						IBA	21.5	0.75
			MP	23.1	0.81			
			DMF	24.8	0.82			
EMA, $\delta = 17.0 \times 10^3$ $(J/m^3)^{1/2}$ (10), $k'_{bulk} = 0.74 \times 10^{-3} s^{-1}$ (11)								
			D	20.5	0.77			
						IBA	21.5	0.84
			MP	23.1	0.89			

It can be seen that for identical polymerization conditions the composite rate constants k' increase with increasing solubility parameter of the solvent, regardless of the strength of the hydrogen bonding parameter. Only k' for the polymerization in BA solution fall out of this observation. k' are for *polymerizations in solvents, which have higher solubility parameters than monomers, higher as k´ for bulk polymerization.*

CONCLUSIONS

The initial rates and especially the maximal rates of polymerization in the gel effect region are in solution polymerization dependent on the solubility parameter of the solvent, i.e. the maximal rates of polymerization and the quotient between maximal and initial rates decrease with increasing value of the solubility parameter.

The influence of the solvent on the polymerization enthalpies of MMA and EMA was not observed.

The composite rate constants in solution polymerization increase with the increasing solubility parameter of the solvent. In cases when solvents have higher solubility parameters than monomers, the constants in solution polymerization are higher than the constants in bulk polymerization.

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