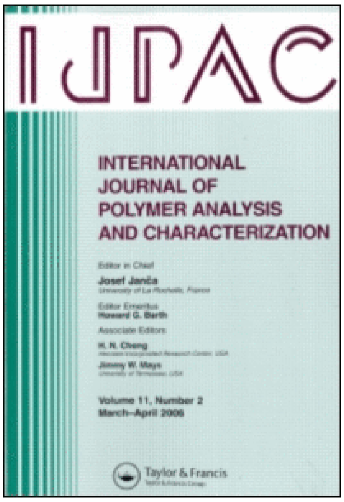

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Kinetics of Radical Polymerization at High Conversion I. GPC Measurements of Molecular Mass Distribution

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A series of poly(methyl methacrylate) (PMMA) samples was prepared with different monomer concentrations and to different degree of conversion in benzene, at 50°C. Average molecular weights and intrinsic viscosity values in the eluent (THF) measured by GPC using an online viscometer are reported. At monomer concentrations up to 50 mol %, no gel effect is observed even in the case of very high conversions (~90%); both molecular weights and kinetic parameters which determine the length of the polymer chain remain practically unchanged independent of conversion. From monomer concentrations of 75 mol %, significant increase of both of these values is observed depending on conversion. The average branching numbers of polymer chains for all samples remain close to zero. The polydispersity values are generally near 1.7. These results denote that there is no significant chain transfer to polymer and the disproportionation probability in chain termination reactions agree with earlier results described in the literature.

Keywords: Molecular weights distribution (MWD), intrinsic viscosity, polydispersity, high conversion, gel effect, poly(methyl methacrylate)

INTRODUCTION

For the production of polymers on an industrial scale, there is an economic need to achieve as high a conversion as possible. This requirement is limited by the phenomenon of autoacceleration [1,2] of polymerization

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reactions at high conversions, commonly called the "gel effect". In extreme cases, it can lead to the thermal explosion of the polymerizing system. This problem has been investigated by several authors [3], often using methyl-methacrylate (MMA) polymerization as a model reaction. Since it is difficult to follow the elementary processes of radical polymerization in the region of high conversions, a satisfactory kinetic interpretation of the "gel effect" phenomenon is still needed. The most probable reason for autoacceleration of a reaction at high conversion is an increase of viscosity and consequently, a decrease of the chain termination constant [4,5].

It has been shown at low conversions that in the polymerization of MMA the kinetic chain transfer to polymer decreases with an increase of molecular mass of PMMA added to the reaction mixture. That means that chain transfer concerns mostly the unsaturated end groups of the polymer molecules [6]; its contribution to branching may be considered negligible also at high conversions. The mechanism of chain termination includes both recombination and disproportionation of radicals [7-10]. Selecting a solvent which at 50°C is practically neutral as a chain-transfer agent [6,11], we followed the characteristics of the products with respect to both monomer concentration and degree of conversion.

EXPERIMENTAL

Radical polymerization of methyl-methacrylate was performed by the dilatometric method in solution of the monomer in benzene at five different concentrations embracing a broad range of 25–90 mol %. AIBN was used as the initiator. The experimental conditions and some kinetic data for the conversions [12,13] are presented in Table I. (For the initial monomer concentration up to 0.50 mole fraction, these kinetic data have been estimated earlier [12] at 50°C from a low conversion experiment with identical results.) The reaction was stopped at conversions from about 5–10% up to values, where it was possible, of 60–88%.

Average molecular weights and intrinsic viscosities were measured using THF as the eluent in a GPC system consisting of five ultraStyrogel columns (10^6 Å, 10^5 Å, 10^4 Å, 10^3 Å and 500 Å was used), Waters pumping (model 500) and injection (model U6K) system, and a Viscotek dual detector (RI/DV, model 200). The evaluation of chro-

Table I Polymerization conditions and kinetic parameters (MMA/BZ/AIBN/50°C)

Sample No	*Time of Reaction (min)*	*Degree of Conversion '(%)*	*AIBN Concentr $x10^2$ (mol/L)*	*Monometer Concentr. (Mole Fraction)*	$k_2/\sqrt{k_4}$ *[mol$^{-1/2}$ dm$^{1/2}$ min^{-2}]*	$2k_tfx10^4$ *[min^{-1}]*
					data according to[12&13]	
			I.			
1	60	5.4	1.48	0.26	0.635	
2	100	9.8			0.638	
3	230	20.8			0.639	
4	350	29.5			0.633	
5	460	36.9			0.635	
6	635	46.8			0.639	
			II.			
1	65	7.0	1.90	0.52	0.630	
2	145	15.0			0.679	
3	260	25.0			0.644	
4	380	35.0			0.662	
5	530	45.5			0.770	
6	750	62.1			1.049	
			III.			
1	210	20.7	1.91	0.53		1.78
2	450	39.4				
3	600	50.2				
5	900	89.6				
6	1110	88.9				
			IV.			
1	220	15.0	0.79	0.75	0.647	
2	380	25.0			0.788	
3	495	35.2			1.707	
4	547	44.9			4.590	
5	573	55.0			9.910	
6	595	64.0				
			V.			
1	115	10.3	1.35	0.90	0.666	
2	225	20.2			0.848	
3	260	24.9			1.196	
4	281	30.0			1.450	
5	297	34.6			2.940	
6	297	35.4			2.940	

matograms was accomplished using universal calibration with 18 polystyrene standards; their hydrodynamic volumes estimated directly from the Viscotek detector.

Particular attention had to be paid to precise adjustment of injected sample concentration, both in the case of standards and investigated materials. Errors in concentration strongly influenced the intrinsic viscosity values. Since the polymer solutions prepared for GPC have to be filtered (Millipore

FHLP filters, 0.5-μm pore size), the risk of concentration errors was a concern. This risk was diminished by preparing at least five times higher amount of sample solutions than those generally used when working with a differential refractometer (2–10 mg of the sample was dissolved in 10 mL of THF, 100 μL was injected). In the case of PMMA chromatograms, the concentration input was corrected by the concentration calibration procedure included in the Viscotek software.

The GPC calibration curve (prepared without filtering standard solutions) has been checked by evaluating the molecular weights of the standards, which were reproduced within ±5% of their nominal values. The best way of checking the results of the molecular weights of PMMA was to inspect the graph of log[η] vs. logM according to the Mark-Houwink equation ($[\eta] = KM^a$). In the case of properly made measurements, straight lines for samples should overlap and the respective parameters K and a should remain in good agreement. These parameters may eventually show some discrepancy, brought about by temperature or elution flow rate fluctuation, minor deviations in the base line of the chromatograms, and/or by the presence of micro air bubbles retained in the viscosity detector reservoirs even after degassing. However, it has been shown from our previous results[14] that the values of K, a pairs show interdependence in this case: they cluster along a straight line, which may be described by the empirical equation $\log K = C - Ba$ (C and B are experimental coefficients). In the case of measurements made in different solvents for the same polymer, such interdependence had been noticed by Mahabadi and O'Driscoll [15]. If the universal calibration curve and two pairs of coefficients of this equation for two a values differing from each other by 0.1 are used for evaluating the same chromatogram, the results obtained in number-average and weight-average molecular weights will differ by no more than 1 and 6%, respectively [14].

RESULTS AND DISCUSSION

The results of GPC measurement, the average molecular weights and average intrinsic viscosity values are presented in Table II and in Figures 1–3. It can be seen that up to the monomer concentration of 50 mol % both intrinsic viscosities and average molecular weights of the samples remain practically constant in the range of conversion from 25 to 88%. A slight descending trend can be observed at conversions below 25%. At 75 mol %

TABLE II Average values of molecular masses and intrinsic viscosities of PMMA samples as measured by GPC

Sample	*$M_n \times 10^{-3}$ ±15%*	*$M_w \times 10^{-3}$ ±10%*	*M_w/M_n*	*[η] (THF) ±6%*	*Degree of Conversion (%)*
			I.		
1	183.2	313.6	1.712	0.548	5.4
2	155.7	282.9	1.816	0.558	9.8
3	119.8	211.4	1.764	0.559	20.8
4	118.7	208.4	1.755	0.532	29.5
5	115.5	200.1	1.732	0.521	36.9
6	116.3	202.1	1.737	0.481	46.8
			II.		
1	249.1	459.0	1.842	1.059	7.00
2	223.4	391.7	1.753	1.011	15.00
3	189.2	324.3	1.713	0.996	25.00
4	193.1	327.0	1.694	0.922	35.00
5	165.1	292.6	1.771	0.940	45.50
6	170.6	327.5	1.919	0.898	62.10
			III.		
1	217.5	376.7	1.730	0.975	20.70
2	183.4	305.5	1.666	0.908	39.40
3	186.2	320.9	1.723	0.890	50.20
4	189.9	340.3	1.792	0.946	68.90
5	226.5	395.3	1.745	1.053	89.60
6	205.5	368.4	1.793	1.091	88.90
			IV.		
1	405.6	702.6	1.732	1.684	15.0
2	478.1	801.4	1.676	1.857	25.0
3	590.8	983.8	1.665	1.887	35.2
4	597.0	1057.0	1.770	2.022	44.9
5	628.2	1098.3	1.748	2.348	55.0
6	682.3	1216.0	1.782	2.417	64.0
			V.		
1	542.3	1168.0	2.153	1.899	10.3
2	659.1	1423.0	2.159	1.984	20.2
3	587.8	1208.0	2.055	1.748	24.9
4	655.1	1204.0	1.837	2.182	30.0
5	741.6	1330.0	1.793	2.048	34.6
6	665.0	1282.0	1.928	2.165	35.4

of monomer concentration an increase of both viscosity and average molecular weights is observed above a 15% conversion. The polydispersities remained practically constant for all samples polymerized from solutions of initial monomer concentration considered so far.

For the last series of the samples prepared at a monomer concentration of 90 mol % the polydispersity was no longer stable. The increase of molecular weights is so high that the GPC investigation in this case is limited by

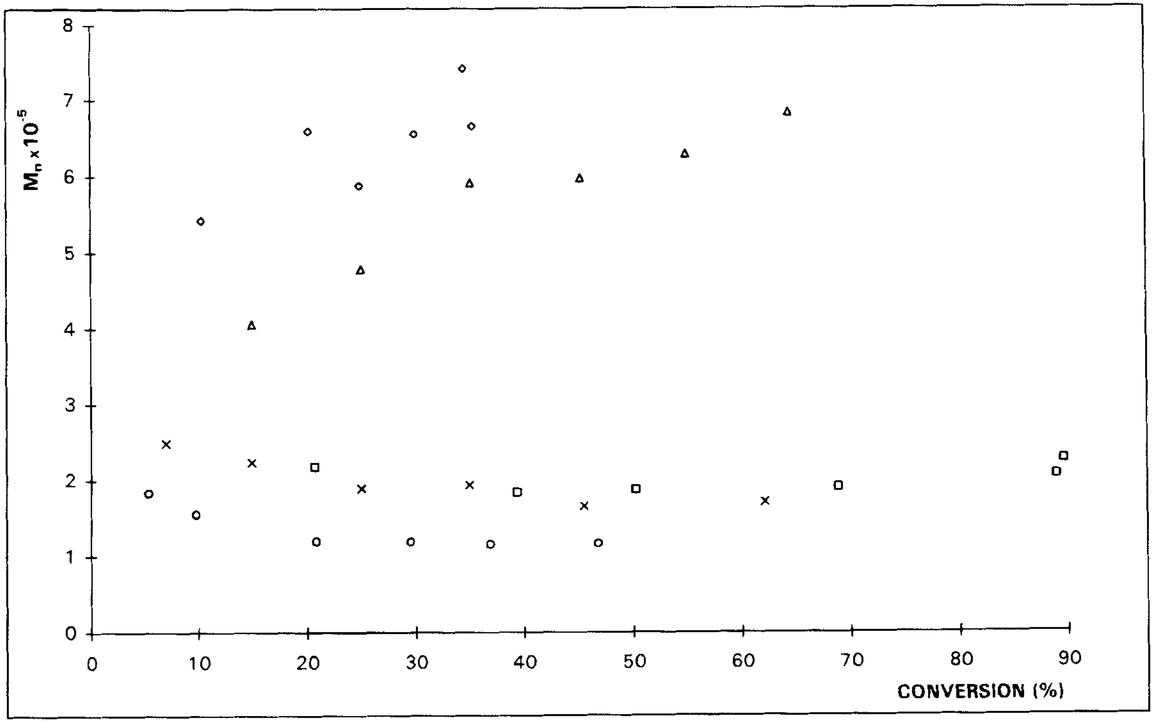

FIGURE 1 Dependence of number-average molecular weights on conversion and initial monomer concentration in benzene (mole fraction): ○: 0.26; x: 0.52; □: 0.53; △: 0.75; ◊: 0.90.

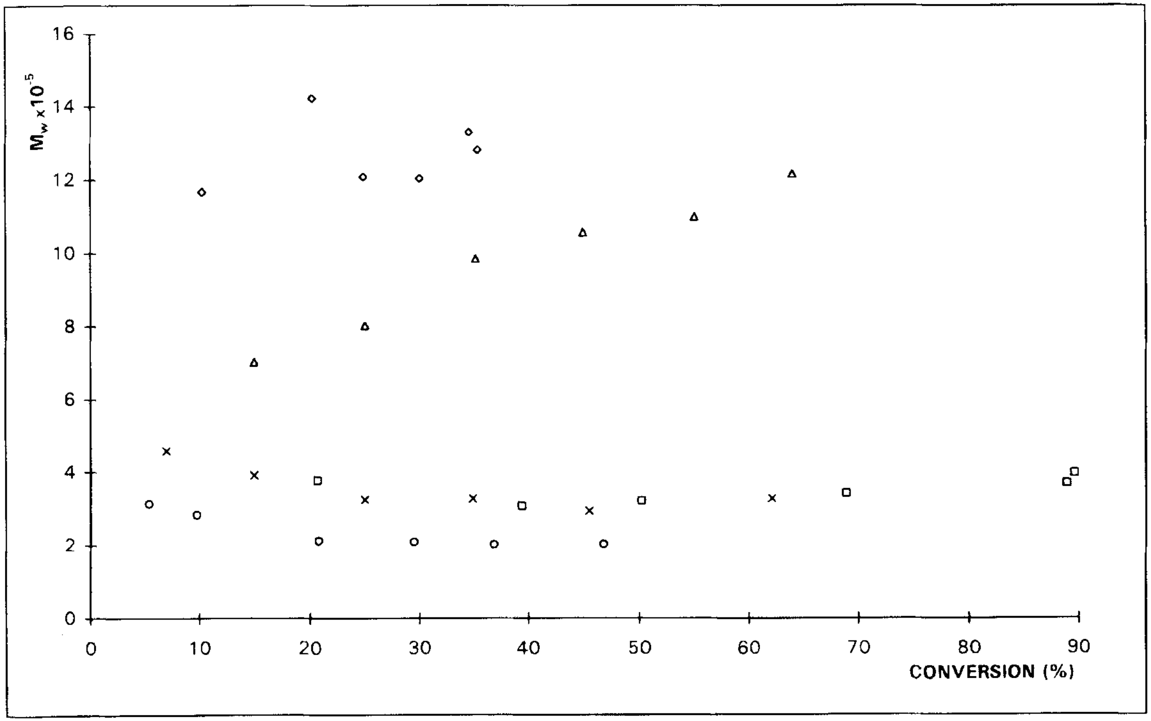

FIGURE 2 Dependence of mass-average molecular weights on conversion and initial monomer concentration in benzene (mole fraction): ○: 0.26; x: 0.52; □: 0.53; △: 0.75; ◊: 0.90.

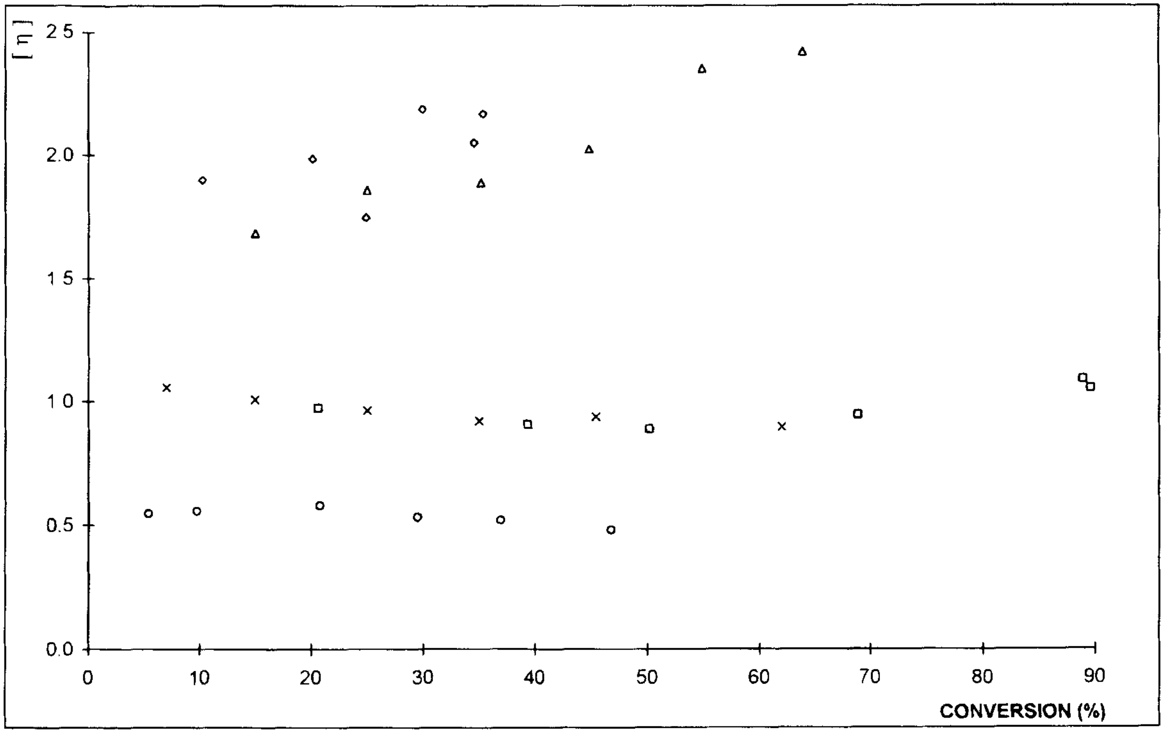

FIGURE 3 Dependence of average [η] on conversion and initial monomer concentration in benzene (mole fraction): ○: 0.26; ×: 0.52; □: 0.53; Δ: 0.75; ◇: 0.90.

the resolution of the columns. Moreover, filtering the solutions of polymer samples of this series was prevented by their high viscosity, and the filters were clogged by the extremly high-molecular-weight samples. The GPC peaks of samples 1–4 of this series show a slightly deformed shape, while for samples 5 and 6 they are perfectly unimodal, which is the reason for the significant spreading of data points observed in this case. For this reason, the data concerning the PMMA samples polymerized in the solutions of 90 mol % of monomer and included in Table II and in Figures 1–3 may be considered only as approximate.

Using Viscotek software for branching estimation based on the Zimm-Kilb theory [16] and the Mark-Houwink parameters [17,18] of linear, polydisperse PMMA sample solutions in THF at 25°C ($\log K = -5.066$, $a = 0.887$), we could show prove that there are practically no long-chain branches in the samples polymerized to high conversions: The number-average values of the long-chain branching for 1000 chain units was in all cases lower than 0.05. The K and a parameters for the Mark-Houwink equation from the literature coincided with the data evaluated for different chromatograms by direct viscosity estimation of the eluted homologous components at the same solute/eluent system and temperature (25 °C ± 1.5), using the GPC Viscotek software. (Fig. 4). However this pair of coef-

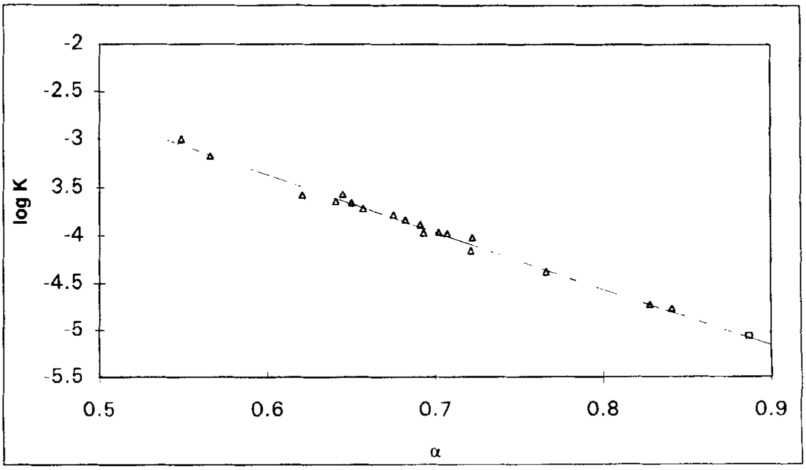

FIGURE 4 Log K vs. a relationship for poly(methyl methacrylate) in THF at ambient temperature (25 ± 1.5°C); Δ: data from the evaluation of the viscosity chromatograms determined by the Viscotek detector; □: from joint data of refs. 12 and 13.

ficients lies apart from the range of K,a pairs of the highest occurrence ($0.6 < a < 0.7$). In fact a value as high as 0.887 was obviously overestimated according to polymer solution theory [19]. We have repeated the determination of branching numbers for all samples using $\log K = -3.972$ and $a = 0.692$ as an average from all our measurements made by the Viscotek detector. The number-average values of branching numbers proved somewhat higher in the case of the samples polymerized in solutions of the highest monomer concentration (90 mol %), but even in this case they remained below the value of 0.3. This was caused by the exclusion of the highest polymer molecules from the chromatographic columns, rather than from branching. Accordingly the kinetic chain transfer to polymer can be practically neglected even at the highest conversions.

In the total conversion range the polydispersity factor is kept constant: $M_w/M_n \approx 1.75$. According to the literature [6], the probability of disproportionation in chain termination for methyl methacrylate at low conversions (10%), at 60°C is $\lambda = 0.61$. Our results show, that it is the case also at high conversions.

CONCLUSIONS

Up to the concentration of 50 mol % of monomer in benzene, the radical polymerization process of MMA performed at 50°C can be easily controlled even in the case of conversions as high as 90%. Both molecular weight and polydispersity can be controlled and obtained easily in diluted MMA polymerization systems with inert solvents.

The gel effect appears at monomer concentration of 75 mol % above 15% conversion. A dramatic increase of molecular weights in this region indicates the appearance of the gel effect and confirms the involvement of chain termination rate under viscosity control. According to theoretical expectations, the probability of disproportionation in chain termination is similar to that at low conversion. The chain transfer to polymer can be neglected.

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