Cross-Linking of Poly(methyl methacrylate) by Aminolysis of Ester Functions with Diamines

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SYNOPSIS

The cross-linking of poly(methyl methacrylate) (PMMA) macromolecules by primary aliphatic diamines was carried out at 413–473 K, above the polymer glass transition temperature. The spherical grains of the suspension-prepared polymer (0.25–0.8 mm) and the molar ratio to amine above 20 were used. The reaction is characterized by an induction period before the macroscopic gel was observed and by fast network formation. Both phenomena are temperature-dependent (87 ± 2 kJ mol^{-1}). The rate of gelation is dependent also on the type of diamine; the shorter induction period of gelation and the higher rate of cross-linking were observed when amino groups were separated with longer alkyl chains. From the kinetics of amine uptake with PMMA, however, it can be concluded that gel formation is influenced also by the reactivity of amine in the transamination reaction and by the amount of bounded diamine. Aminolysis of PMMA ester groups proceeds from the very beginning of heating of the reaction charge. The polymer cross-linking prevails when there is more than 60% of diamine attached to PMMA in dependence on the amine type used. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The growing variability of macromolecular chemical procedures in the polymer melt increases the interest in chemical reactions of polymers and the preparation of polymers with new properties. For example, the reactive processing of polymers is a fast-developing technology based on solvent-free polymer-analogous reactions.[1-4] The variability, high reaction rate, ecology, and low cost of molten-state polymer reactions are some of the main reasons why both science and industry find them of interest.

The acrylic and methacrylic acid ester polymers are transformed to new materials very often by chemical reactions that involve the ester groups. The aminolysis reaction proceeds with NH_3 or primary amines under pressure and alkaline catalysis at high temperatures.[5] These reactions bring new functionalities to poly(methacrylic ester)s macromolecules. Nevertheless, the transesterification or transami-

nation of poly(methyl methacrylate) has been known for a long time[5,6]; intensive studies have been carried out with respect to catalytic mechanisms, kinetics of the exchange reaction, and the degree of conversion.[7,8] With the aim to prepare water-soluble poly(methyl methacrylate), Zilberman and co-workers treated beads of the suspension polymer with an excess of ethanolamine.[9] At 443 K, a maximum of 37% of poly(methyl acrylate) beads modified with multifunctional amines were prepared as possible drug-delivery systems,[10] floculants,[11] adsorption materials, ion-exchanger resins, and materials for chromatography.[12,13]

The reaction is mostly performed with a great excess of amines[8,10,12] in the solution or highly swollen porous polymer beads. Acrylic or methacrylic ester copolymers with the other vinyl monomers are very often used as the basic macromolecular backbone. Recently, the aminolysis of poly(styrene-co-methyl acrylate) in solution has been compared to the one in the melt.[7,8] In an extruder, the conversion was only around 4% at 493 K and 150 s residence time. The solution reaction was higher but always limited to less than 40% despite the high concentration of reactants, high temperature, and the long

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reaction time. A comparison of the rate constants shows that there is no difference between aminolysis in polymer solution and in bulk polymer.

The catalytic effect of lead and zinc on the reaction of amino alcohols with poly(methyl methacrylate) has been studied by Khitrin et al.[11] The reaction conditions for the preparation of copolymers bearing an optional concentration of oxyamide and aminoester groups were presented.

A particular case of the functionalization is the modification of porous cross-linked polymer particles. Poly(methyl acrylate) beads swollen in dimethylformamide reacted with an excess of multifunctional amines following a simple first-order kinetics.[10] The formation of additional cross-links hampers the reaction rate by affecting the diffusion of amines in the polymer particles. To avoid additional cross-linking and, hence, to obtain polymers with a higher functionality, is best done in the presence of excess amine.

In the most of the transamination studies of acrylate and methacrylate polymers, the cross-linking is considered as an undesirable reaction. Nevertheless, the macromolecular network in some cases improves the physicomechanical properties of the polymeric material.[14] For example, poly(methyl methacrylate)-based materials have good mechanical properties. The MW needs to be greater than 10^5 g mol^{-1}. However, this is the upper limit to ensure the reasonable rheological properties of polymer melt without remarkable thermal degradation. The possible solution of these contradictory requirements can be found in forming the network by cross-linking of the polymer in the final product or during its processing.

In this article, we present studies of the kinetics of poly(methyl methacrylate) cross-linking using polymer/analogous reactions with small concentrations of aliphatic diamines. We were interested in the kinetics of the transamination reaction without any additives as catalysts or solvents. Suspension poly(methyl methacrylate) beads (injection-molding-type polymer) were reacted at temperatures above the glass transitions.

EXPERIMENTAL

Materials

The polymer poly(methyl methacrylate) (PMMA) was suspension polymerized methyl methacrylate supplied by PCHZ Chemical Works, Slovakia. The size distribution of polymer beads used in the cross-linking experiments is presented in Table I. Polymer with particle diameters of 0.25–0.8 mm was used. The average molecular weight of PMMA from the viscosity was 1×10^5 g mol^{-1}.

Aliphatic diamines 1,3-diaminopropane (1,3-DAP) 1,6-diaminohexane (1,6-DAH), and 1,12-diaminododecane (1,12-DAD) were Fluka chemicals of analytical-grade purity. These compounds were used as obtained as well as were solvents for impregnation (ethanol) and extraction of soluble polymer from the reaction products (chloroform).

Reaction Conditions

The reaction was carried out in sealed glassy ampules under a nitrogen blanket in the molten state (above the glass transition temperature of PMMA). The free space in ampules represented $\frac{1}{3}$ to $\frac{1}{4}$ of the whole volume. Reaction temperatures were 413, 433, 453, and 474 K. The concentration of diamines was low: 0.108 mol kg^{-1}. Samples for the determination of the reacted amine were cross-linked with 0.5 mol kg^{-1} of diamine.

The reaction feed consisted of PMMA beads impregnated with diamine. Concentrated ethanol solution of amine was poured on PMMA grains, mixed vigorously together, and allowed to evaporate the solvent in a gentle air stream. This operation takes about 45–60 min. One gram of impregnated polymer was filled in each ampule.

Analysis

A dissolution of the reaction product in chloroform was used to determine the conversion of PMMA polymer to the insoluble macromolecular network. The extraction was carried out at the laboratory

Table I   The Size Distribution of PMMA Beads Used in Cross-linking Experiments

	Particle Diameter (mm)					
	< 0.250	0.250 0.315	0.315 0.400	0.400 0.630	0.630 0.800	> 0.800
Amount of fraction (%)	1.8	10.4	34.2	21.6	25.8	6.2

temperature with 25 times the excess of the solvent, which was exchanged for three times during 5 days.

The content of bounded diamine was determined as the amount of nitrogen in the polymer using the CHN elemental analyzer Heraeus. Before analysis, the soluble as well as the gel fraction of the modified polymer were carefully freed from unreacted diamine by extraction and precipitation.

As the reactants were mixed together at a temperature below the glass temperature of PMMA grains, the diffusion of amine from the surface to the core could hamper the rate of the reaction, although this will be valid only if diameters of the particles are larger than 0.8 mm (Table II).

RESULTS AND DISCUSSION

The chemical reactions of linear macromolecules with multifunctional compounds lead progressively from increasing the polymer molecular weight to insoluble cross-linked networks. Consequently, sol–gel analysis is often used for the following the cross-linking process. The rate of polymer network formation is evaluated as the weight increase of the insoluble gel fraction in the sample. However, this so-called rate of gelation is not identical with the rate of the polymer-analogous transamination of PMMA ester functions. Comparing the appearance of the gel fraction with the nitrogene content in the sample, we are able to show the differences between these two processes.

The analysis of polymer cross-linking shows that at least one cross-linking, on average, is needed to observe the gel point in the polymer with the most probable distribution of molecular weights.[15] In this study, the predominant ratio of MMA links to diamine was 100. So, for PMMA with a degree of polymerization of 1000 used in the experiments, there can be 10 times more amine molecules required for

Table II   The Influence of PMMA Bead Size on the Rate of Its Gelation During the Transamination Reaction with 1,3-DAP (1,130 mol kg^1) at 433 K

	Particle Size (mm)			
	< 0.25	0.25–0.8	> 0.8	3[a]
Gelation[b] (%/h)	31	30	23	0

[a] Cube with 3 mm edges.
[b] Average rate to 2.5-h reaction without an induction period.
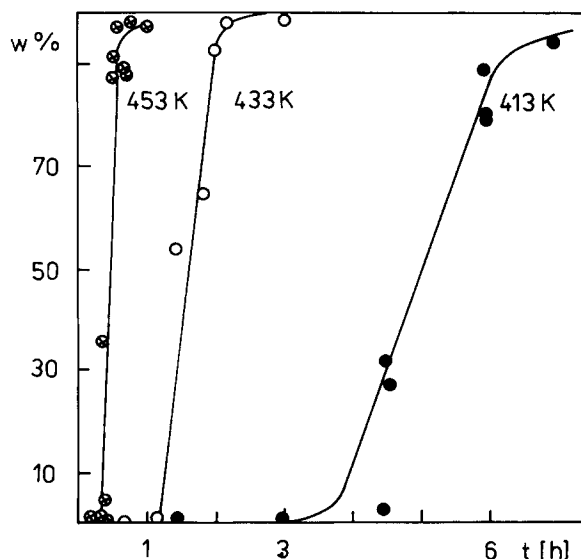
Figure 1   The amount of cross-linked polymer in the PMMA sample during its transaminations with 1,6-DAH (0.108 mol kg^{-1}) in dependence on temperature and time of reaction.

PMMA macromolecule gelation provided that the reaction proceeds at random with sufficient conversion.

The minimum concentration of diamine can be anticipated under which only addition proceeds and the gel point cannot be achieved. This situation depends foremost on the PMMA molecular weight and its distribution.

Cross-linking During Aminolysis

The shape of time dependencies of a macroscopic gel formation in the reaction of PMMA with diamines is characterized with induction periods and fast transformation of the whole polymer to an insoluble network (Figs. 1–3). Both the time of induction and the rate of gelation are strongly influenced by the temperature of the reaction. By plotting these values in Arrhenius coordinates (Fig. 4), we can evaluate the temperature coefficient E_g of the cross-linking process during the transamination of PMMA with diamines. For the temperature range 413–453 K, we determined $E_g = 87 \pm 2$ kJ mol^{-1} for all three diamines studied.

The rates of gelation of the PMMA during transamination reactions with aliphatic diamines as well as the induction periods until an observable gel is formed are presented in Table III. Referring to these values, the induction periods of gelation and the rates of gelation depend on the size of amine mol-
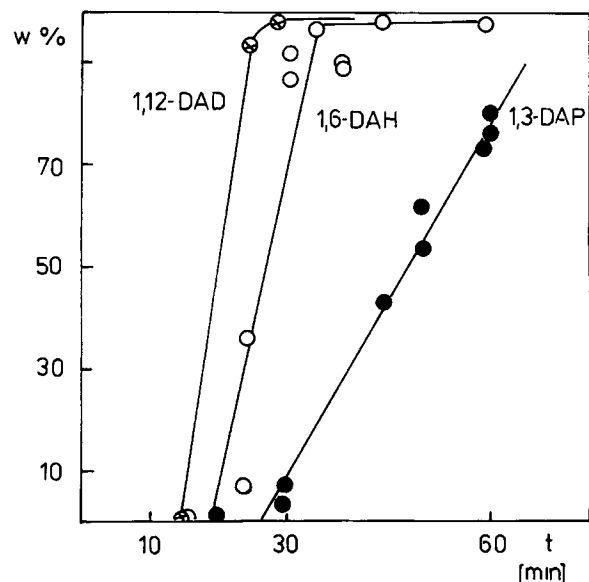
Figure 2 The amount of cross-linked polymer in the PMMA sample during its reaction with various diamines (0.108 mol kg^{-1}; 453 K) in dependence on time of reaction.

ecules. Large molecules, 1,6-DAH and 1,12-DAD, reacted faster in linking PMMA macromolecules compared to 1,3-DAP. For example, the amount of the gel in the sample of PMMA during the reaction with 1,3-DAP (0.108 mol kg^{-1}, 453 K) increases at the rate of 2.4 wt % in 1 min. The macroscopic ge-
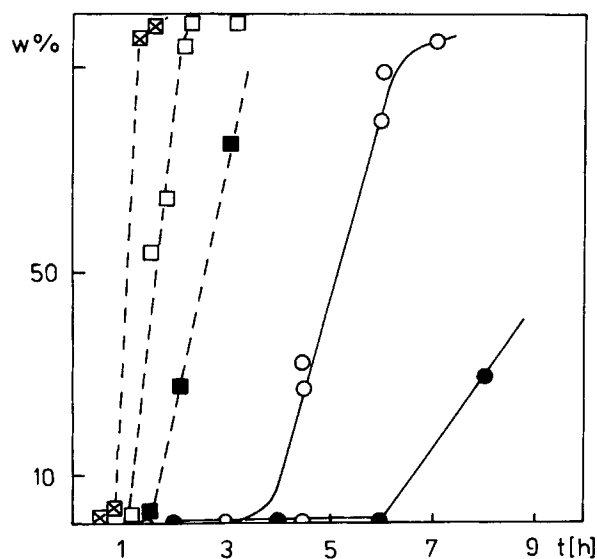
Figure 3 The amount of cross-linked polymer in the PMMA sample during its transamination reaction in dependence on time of reaction and on type of diamine used. 413 K: (●) 1,3-DAP; (○) 1,6-DAH. 433 K: (■) 1,3-DAP; (□) 1,6-DAH; (⊠) 1,12-DAD.
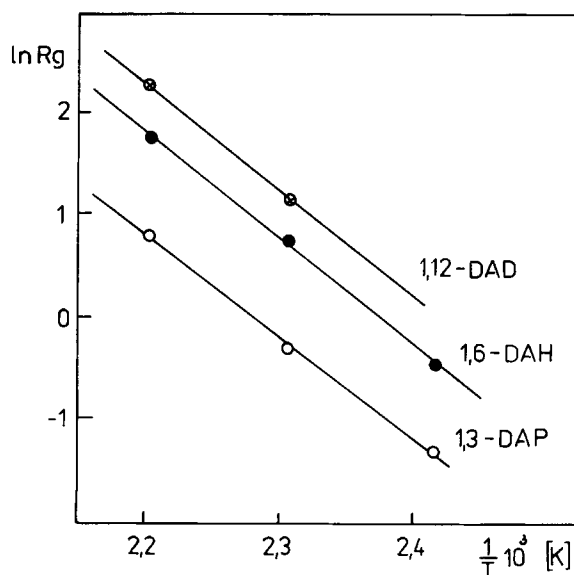
Figure 4 The rate of PMMA gelation during the transamination reaction with aliphatic diamines in dependence on reciprocal values of temperature; concentration of diamines: 0.108 mol kg^{-1}.

lation started approximately after 26 min. At the same experimental conditions, the PMMA cross-links with 1,12-DAD five times faster, the induction period to the gel appearance being only 14 min (Fig. 2). From these facts, one can assume that a prolonged spacer of bonded diamine favored the reaction of its second amine group with ester functions of other PMMA macromolecules. So, if 1,3-DAP was used in the reaction, the slowest gelation of PMMA would not be surprising. The highest rate of gelation

Table III   Induction Periods Until Observable Gel is Formed and the Rates of Gel Formation During PMMA Transamination in Dependence on Temperature and Diamine Used in the Reaction (Concn of Diamine: 0.108 mol kg^{-1})

Temperature (K)	1,3-DAP	1,6-DAH	1,12-DAD
Induction period (min)			
413	360	220	—
433	90	70	50
453	36	19	14
Rate of gel formation (wt % min^{-1})			
413	0.26	0.60	—
433	0.73	1.64	3.20
453	2.30	6.20	9.90

of PMMA with 1,12-DAD corroborates also with our consideration that in the presented experiments the diffusion of reactants is not the reaction-limiting process.

Bounding Diamines to PMMA

As can be seen from the dependencies presented in Figure 5, the transamination proceeds from the beginning of the thermal treatment of the reaction mixtures and also in the time of the induction periods observed from the dependencies of the gel content in the samples on the time of the reaction (Figs. 1–3). The absence of gel in this period shows that transamination consumes predominantly only one of diamine groups. Later, the modified PMMA macromolecules with pendant amido–amine functions are cross-linked, involving in the reaction the second amino groups of bounded α,ω-diamine. Such features of the transamination kinetics of PMMA with 1,3-DAP, 1,6-DAH, and 1,12-DAD, namely, the very late start of the gelation, led to the conclusion that the amino group in low molecules are considerably more reactive than are the amino groups bounded to less mobile PMMA macromolecules.

The dependencies of the nitrogen content in the reacting polymer on the time of reaction (Fig. 5) were used for calculation of the reaction rate con-
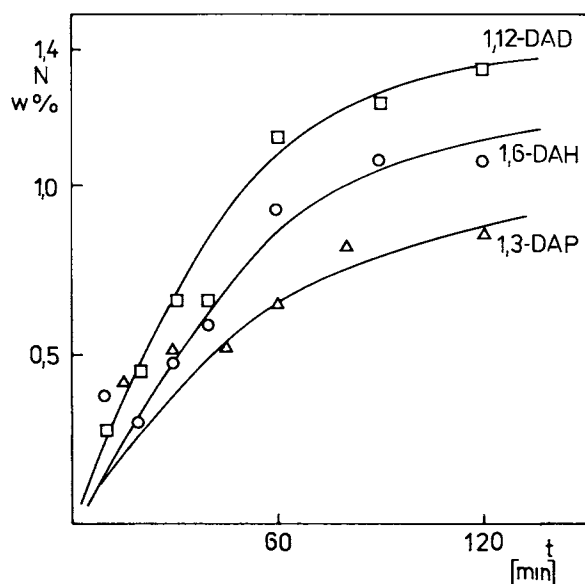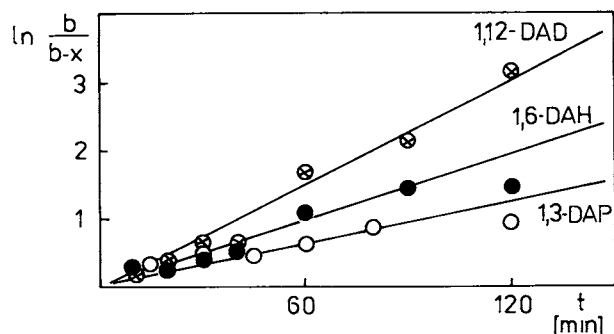
Figure 6   The uptake of nitrogen during transamination of PMMA presented as a pseudo-first-order reaction; diamine: 0.5 mol kg^{-1}, 433 K.

stants. The low molar ratio (0.05) of the diamine to MMA units in PMMA allows us application in the calculation of pseudomonomolecular evaluation of this bimolecular reaction. Plots in Figure 6 are linear, which confirms that the amount of nitrogen bonded to PMMA fulfils the first-order kinetics. At 433 K, the rate constants $k_1[s^{-1}]$ are 4.23×10^{-4}, 2.70×10^{-4} and 1.73×10^{-4} for 1,12-DAD, 1,6-DAH, and 1,3-DAP, respectively. The straight lines passing through the origin also confirm that transamination proceeds from the very beginning of the reaction without any induction period. The reactivity of the free diamine in the PMMA transamination depends on the length of the spacer between amino groups. The 1,3-DAP reacts slower than do the two other amines 1,6-DAH and 1,12-DAD. This behavior of the reactants can be explained by the different compatibilities of the diamines with PMMA. The estimated cohesion energies on the volume unit increase in the order 1,12-DAD to 1,3-DAP.[16] Seeing that a cohesion energy of PMMA[16] is closest to this quantity of 1,12-DAD, we can expect also the better compatibility of these reactants favoring reactivity in comparison to other couples.

Using k_1 and time of induction periods of gelation, one can calculate the amount of bounded diamine before the gel point. At 433 K and 0.108 mol kg^{-1} of diamine, gelation started when 61, 68, and 72%, respectively, of 1,3-DAP, 1,6-DAH, and 1,12-DAD were bounded to PMMA.

The increasing amount of bounded diamine to the gel point is associated with a different reactivity of respective amines and with a lower reactivity of amino groups of modified PMMA with other PMMA macromolecules. The later gelation, namely, when 1,12-DAD is applied, can be connected also with intramolecular cyclization reactions that are facilitated by the long methylene chain in the amine mol-

Figure 5   The concentration of nitrogen in modified PMMA in dependence on time and type of diamine used in the transamination reaction (diamine: 0.5 mol kg^{-1}, 433 K). A complete bonding of diamine represents 1.4 wt % of nitrogen in PMMA.

ecule. However, we have no experimental proof of such structures.

Nevertheless, the calculated values of diamine bounded to PMMA in the time of the gel point gives the more important information of PMMA diamine cross-linking. In the gel point, there are already six to seven diamine molecules bounded to PMMA as precursors of cross-links. However, there is only one cross-link between two macromolecules, on average, needed to have the gel fraction appear. From this result, it can be concluded that the reactivity of the free diamine is three to five times higher than is the reactivity of amino groups bounded to PMMA.

The determination of nitrogen in the sample of the modified PMMA can be used to study the reaction kinetics only in the first stage of transamination cross-linking of PMMA. To evaluate the reactivity of the second amino group in PMMA cross-linking, it is still possible to use the results of sol–gel analysis. The rate of cross-link formation is identical with the rate of the intermolecular reaction of the second amino group of the bounded diamine and can be calculated approximately from the number of cross-links (γ) using the relationship[15]

$$\gamma = \frac{1}{S + S^{0.5}}$$

where S represents soluble weight fraction of the sample.

This procedure can be practically used up to concentration of five cross-links per macromolecule of
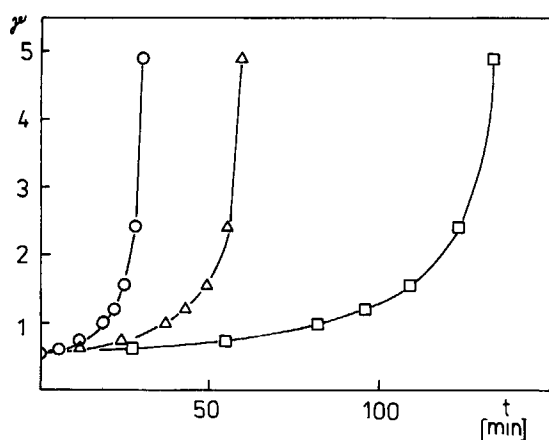
Figure 7 The average number of cross-links γ in dependence on the time of PMMA gelation during the transamination reaction with aliphatic diamines; 433 K; concentration of diamines: 0.108 mol kg^{-1}: 1,12-DAH (O); 1,6-DAH ($\triangle$); 1,3-DAP ($\square$).

the parent polymer. As a rule, this means that the cross-linking can be followed starting with the gel point to ca. 97% polymer conversion to the insoluble network.

In the experiments (Fig. 1–3), the content of the gel grew linearly with respect to accuracy of the gel determination. With respect to the relation between the gel fraction and γ, the rate of cross-link formation involving PMMA-bounded amino groups is accelerated with increased cross-linking density (Fig. 7). PMMA modified with 1,12-DAD at 433 K reacts at the highest rate and it takes 31 min to reach 97% gel content and $\gamma = 4.9$ in the sample.

At the same experimental conditions, $\gamma = 4.9$ for 1,6-DAH is reached after 61 min and after 137 min for 1,3-DAP. Though the PMMA cross-linking is complex during transamination, the experimental results show that prolonging of the methylene spacer in γ,ω-aliphatic diamines makes them more reactive in both steps of the network formation.

CONCLUSIONS

In comparison with the formation of cross-linked PMMA-based polymers in the copolymerization of MMA with multifunctional vinyl monomers, the course of the network formation during transamination with diamines is characterized by a relatively long induction period until macroscopically observable gel is formed: The determined temperature dependence of the rate of gelation (E_g) shows that at 373 K the T_g temperature for injection-molding types of PMMA, the 80% conversion to insoluble polymer can be achieved in 55 h. The same cross-linking extent of PMMA at 473 K takes of about 6 min. At 533 K, the cross-linking time is shortened to 30 s, which is comparable with the mean time of the injection-molding cycle in PMMA processing. Since the transamination reaction in the PMMA melt is fast enough and involves, at first, only one amino group of diamine, it can be used as an attractive route to a new polymer in reactive processing technology.

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