Template Polymerization of Methacrylic Acid in the Presence of Poly(*N*-Acetyl Iminoethylene) Macroazoinitiators

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TEMPLATE POLYMERIZATION OF METHACRYLIC ACID IN THE PRESENCE OF POLY(*N*-ACETYL IMINOETHYLENE) MACROAZOINITIATORS

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ABSTRACT

Thorough studies on the polymerization of methacrylic acid in aqueous solution in the presence of poly(*N*-acetyl iminoethylene), macroazoinitiators evidenced a dependence of the polymerization rate on solvent capacity to participate in hydrogen bonding interactions and on poly(*N*-acetyl iminoethylene) chain dimension and concentration. This behavior was ascribed to the template character of the process. The complexation ability of poly(*N*-acetyl iminoethylene) with carboxyl-containing vinyl monomers and polymers was demonstrated by a viscometric technique. A plot of the polymerization rate dependence on the base molar concentration of poly(*N*-acetyl iminoethylene) presents two maxima for [MAA]:[PNAI] ratios of 2:3 and 2:1, similar to the composition of the most stable complexes formed during block copolymerization. This characteristic is presumed to arise from a change of the matrix during the process, i.e., the poly(*N*-acetyl iminoethylene) template is replaced by the poly(methacrylic acid) complexed daughter polymer following the filling of all first template sites.

INTRODUCTION

Template polymerization has been a frequent subject of study in the last 30 years due to scientific and practical interest in developing new methods of polymerization, especially of vinyl monomers, and the manufacture of new materials [1, 2]. As compared to conventional polymerization, template polymerization consists on propagation along template macromolecules as a consequence of cooperative interactions between the growing chain and the template chain. This unusual mode of polymer formation implies changes in the polymerization kinetics and also in structural features of the polymer formed. A careful choice of the matrix allows some control of both the polymerization reaction and the structure of the daughter polymer (chain dimension, stereoregularity, and composition).

The presence of polyethylenimine among the macromolecular templates [1, 3, 4], as well as recent reports on hydrogen-bonded complexes of poly(N-propionyl iminoethylene) with polymers containing phenol or carboxyl groups [5], suggests that poly(N-acetyl iminoethylene) might be used as a template in the polymerization of appropriate vinyl monomers.

Some previous papers reported the synthesis of block copolymers with poly(N-acetyl iminoethylene) and vinyl sequences by solution [6] or by the emulsifier-free emulsion polymerization [7] of different monomers in the presence of poly(N-acetyl iminoethylene) macroazoinitiators. This work is concerned with the polymerization of methacrylic acid initiated by the same macroinitiators. Macromolecular compounds of this type are characterized by structural regularity (highly symmetric backbones with a 2_1 helical conformation) [8, 9]. A supplementary argument for such a choice involves the possible influence on the microstructure of the polymer formed.

EXPERIMENTAL

Materials

Methacrylic acid (MAA) and 2-methyl-2-oxazoline (MOZO), commercial products, were purified by distillation under an inert atmosphere.

1,4-Dibromo-2-butene (Fluka), 4,4'-azobis(4-cyanopentanoic acid) (Aldrich), and N,N-dimethylformamide (DMF) (Merck) were used as received without further purification.

Chloroform and ethanol (anhydrous) were dried by refluxing on P_2O_5 and magnesium and sodium ethoxide, respectively, and distilled. Doubly distilled water was used for the polymerizations.

Poly(N-acetyl iminoethylene) (PNAI) macroazoinitiators were synthesized as previously reported [6] by capping hydroxyl-terminated poly(N-acetyl iminoethylene) of controlled molecular weight [10] with 4,4'-azobis(4-cyanopentanoyl chloride) [11] in the presence of triethylamine (Scheme 1). Their characterization data are listed in Table 1.

Poly(methyacrylic acid) (PMMA) was obtained by polymerization, in toluene, at 60°C with benzoyl peroxide as initiator. Its viscosity-average molecular weight was determined in methanol at 26°C [12].
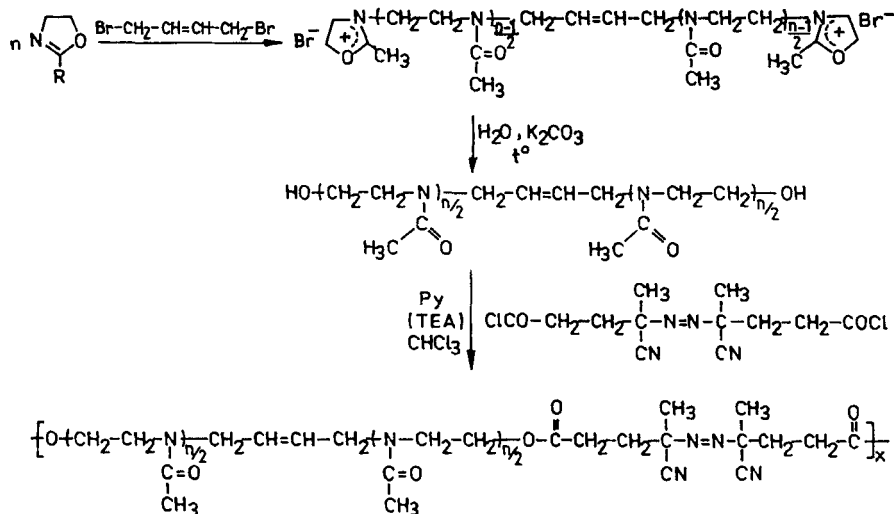
SCHEME 1.

Polymerization

The polymerizations were carried out in sealed glass ampules, under argon, in the conditions mentioned in the text. Small amounts of hydroquinone were added to the reaction mixture at the end of the process in order to avoid further polymerization. The solid products remaining after water removal were repeatedly washed with ethyl ether and methylene chloride to avoid contamination with unreacted monomer or unused macroinitiator. They were dried to constant weight in vacuum at 60°C and kept in a dessicator in the presence of concentrated H_2SO_4. The composition of each sample was determined by elemental analysis for nitrogen and from ^{1}H-NMR spectra.

The rates of polymerization (R_p) were obtained with the relation $R_p = 1000w/vtM$, where w is the weight of the PMAA sequence (g) as calculated from the total yield and composition data, v is the volume of the polymerization system (mL), t is the time of polymerization (seconds), and M is the molecular weight of MAA.

TABLE 1. Macroazoinitiators

Sample	Sample code	[MOZO]/[DBB][a] in feed	$[\eta]$, prepolymer	$[\eta]$, macroinitiator
1	I_{20}	20	3.5	5.3
2	I_{40}	40	4.8	6.9
3	I_{60}	60	5.8	8.8
4	I_{80}	80	6.4	7.3

[a]Polymerization conditions: [MOZO] = 4.7 m, $CHCl_3$, 55°C, Ar, 8 hours.

Characterization

The ^{1}H-NMR spectra were recorded on a Jeol-C-60HL instrument using DMSO-d_6 as solvent Viscometric measurements were performed with an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Complexation Ability of PNAI with MAA and PMAA

The driving force in template polymerization is the ability of two complementary polymers to form stable complexes by H-bonding, charge transfer, or electrostatic interactions.

In order to estimate the complexing capacity of the two polymers involved in the present polymerization process, i.e., PNAI and PMAA, a viscometry technique was used. Figure 1 shows the dependence of the reduced viscosity of the corresponding dilute solutions and their mixtures on the weight composition in three different solvents: water, ethanol, and N,N-dimethylformamide. Deviations from additivity were detected in all cases; strong and negative for the first two solvents, and weak and positive for the last one. This behavior is the consequence of coil shrinkage or of gel formation due to H-bonding between the two polymers, with the participation of HOOC— groups of the polyacid and the carbonyl groups from PNAI. The complexation proceeded fast even for average molar masses as low as 5200 for PNAI and 10,890 for PMAA (Fig. 1).

As is known [2], complementary polymers which show an increase of η_{sp}/c rarely yield a good template system, so that unsatisfactory results were expected for the experiments performed in DMF. The polymerization results confirmed this assumption. Thus, the total polymerization conversions (conditions: [MAA] = 2 m, [PNAI] = 0.8 m, [I_{20}] = 4 × 10^{-2} m, 70°C, 5 hours) decreased in the order
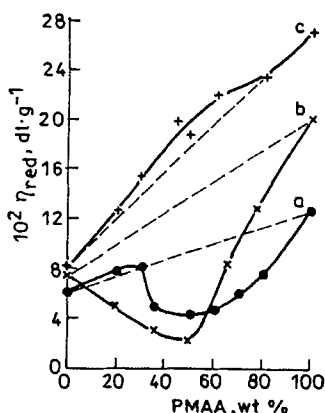

FIG. 1.   Plots of η_{red} vs the weight percent of PMAA for PNAI/PMAA mixtures in (a) water, (b) ethanol, and (c) N,N-dimethylformamide (T = 25°C, c = 0.5 g·dL^{-1}, M_{vPMAA} = 10,890, M_{nPNAI} = 5200).

water > ethanol > DMF (51, 28, and 17%, respectively). Similar results on complexation affinity modification with the nature of the solvent were earlier reported [13] for the poly(methacrylic acid)-poly(vinylpyrrolidone) system. Poly(vinylpyrrolidone), a polymer often used as a template [2], contains substituted amide groups as does PNAI. These data can be explained by the competition between the small solvent molecules and methacrylic acid for the interaction sites of the template (the ethanol case) or with the macromolecular matrix for the monomer (the DMF case). DMF appears to be a potent hydrogen bond acceptor. The MAA-DMF interaction has been demonstrated by viscometric and calorimetric measurements (association heat = 7.5 kJ/mol) by Challa et al. [14].

In aqueous solution, a few minutes after mixing the components of the polymerization system (for the MAA concentrations used in this study), a slight separation of a brown oily product was observed, indicating monomer preadsorption by the PNAI sequences of the macroinitiators. The interaction between MAA and PNAI was also evidenced by viscometry (Fig. 2). The reduced viscosity versus composition plot is nonlinear, with a drop for a 1:1 mole ratio.

Although PNAI and PMAA (except it-PMAA) are individually soluble in neutral water, clear solutions were obtained with mixing only in the very dilute domain. The solutions became hazy or quite turbid when the molecular weights and concentrations of the two components were increased. Thus, it was not unexpected that the polymerization became heterogeneous with time and, depending on the concentration ratio and polymerization technique, eventually resulted in the separation of a gelatinous precipitate. After drying, the last sample became totally insoluble in water, partially soluble in ethanol, and soluble in DMF. Its dilute solution behavior is presented in Fig. 3. The independence of the reduced viscosity on con-
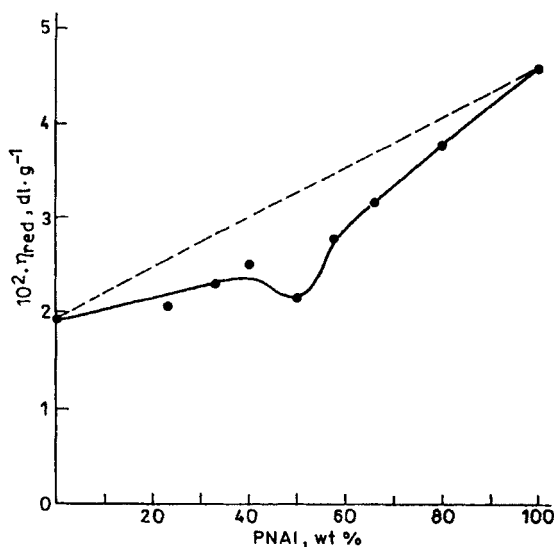

FIG. 2. Reduced viscosity vs weight percent of PNAI for aqueous mixtures of MAA/PNAI ($T = 25°C$, $c = 0.8$ g·dL^{-1}, $M_{nPNAI} = 3700$).
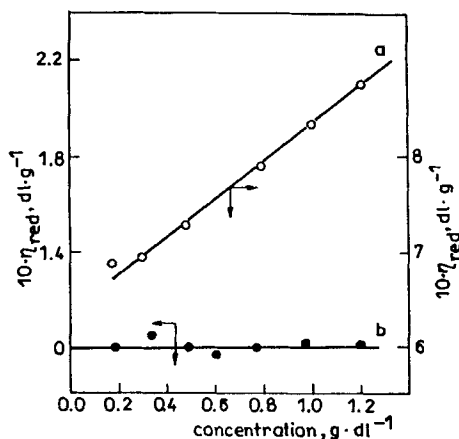
FIG. 3.   Dependence of the reduced viscosity on concentration for the dilute solution of the PMAA-*block*-PNAI-*block*-PMAA copolymer in (a) DMF and (b) ethanol ($T = 25°C$).

centration in ethanol denotes a high compactness of the polymer coil as a consequence of the strong intramolecular interactions in the block copolymer produced.

This behavior is in agreement with the generally accepted fact that in-situ complex formation, i.e., by template polymerization, leads to ladder-type complexes in which a more efficient complexation can be achieved as compared to that attained by simply mixing of the two ready-made polymers.

Polymerization Features

The duality of poly(N-acetyl iminoethylene)-i.e., as a matrix and polymerization initiator—made the choice of a blank polymerization system very difficult. Moreover, the macromolecular character of the initiator lowers its decomposition efficiency as compared to common, low molecular weight compounds with similar
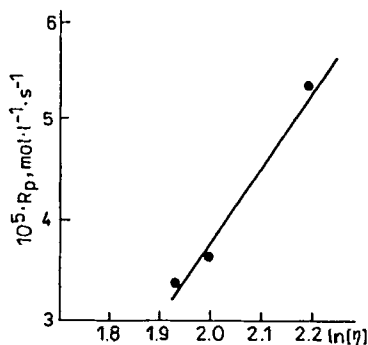

FIG. 4.   Influence of the PNAI macroazoinitiator (template) length on the polymerization rate ([PNAI] $= 1$ basemole·L^{-1}; [MAA]$_0 = 3$ m; $I_n = I_{40}, I_{60}, I_{80}$; $T = 70°C$).
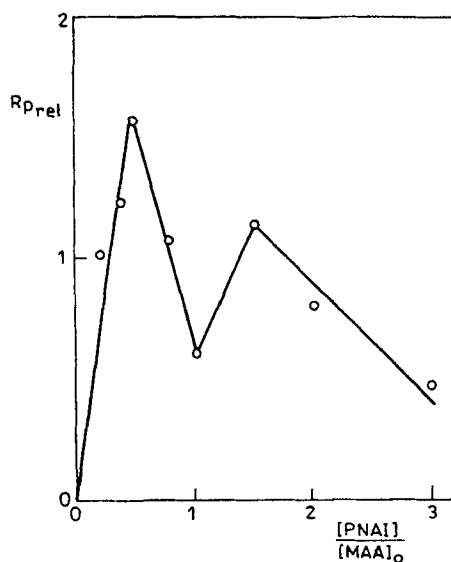
FIG. 5. Relative rate vs [PNAI]:[MAA]$_0$ molar ratio at constant initial monomer concentration ([MAA]$_0$ = 0.5 m, $I_n = I_{20}$, T = 80°C). $R_{P_{rel}} = R_p:R_{p,t}$, $R_{p,t}$ = theoretical value of the polymerization rate considering classical kinetics (i.e., a 0.5 order in initiator) as valid.

chemical structures [6, 15, 16]. Yet, for molecular weights of a limited domain, the polymerization rate was seen to increase with an increase in the length of the macroinitiators and of the PNAI sequences included in their main chain (Fig. 4), in spite of the simultaneous decrease of the content in labile azo groups. As is known [17], the rate decreases with increasing pH in the polymerization of MAA in aque-
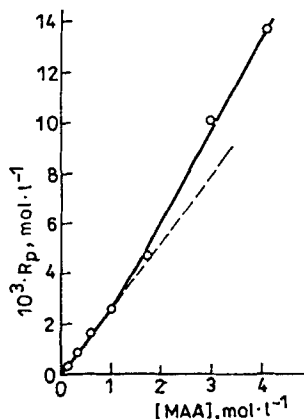

FIG. 6. Polymerization rate of methacrylic acid as a function of monomer concentration at constant PNAI template content ([PNAI] = 1 basemole·L^{-1}, [I_{20}] = 5 × 10^{-2} m, T = 70°C).
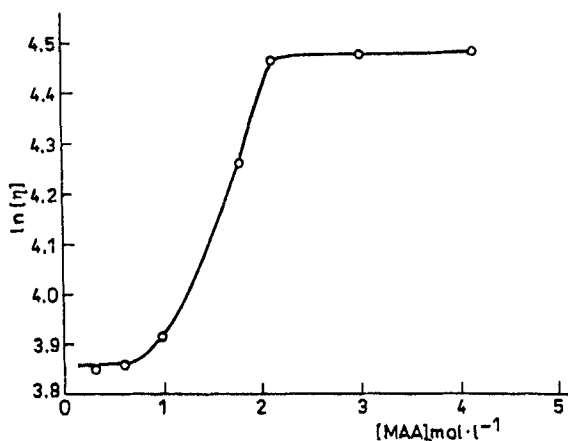
FIG. 7.   Variation of $\ln[\eta]$ against monomer concentration in the feed for the block copolymers produced.

ous media. In the present study the rate was observed to increase with the addition of growing amounts of PNAI (Fig. 5), even though the pH increased from about 2.5 to about 4.5. These aspects point out the template character of the studied polymerization.

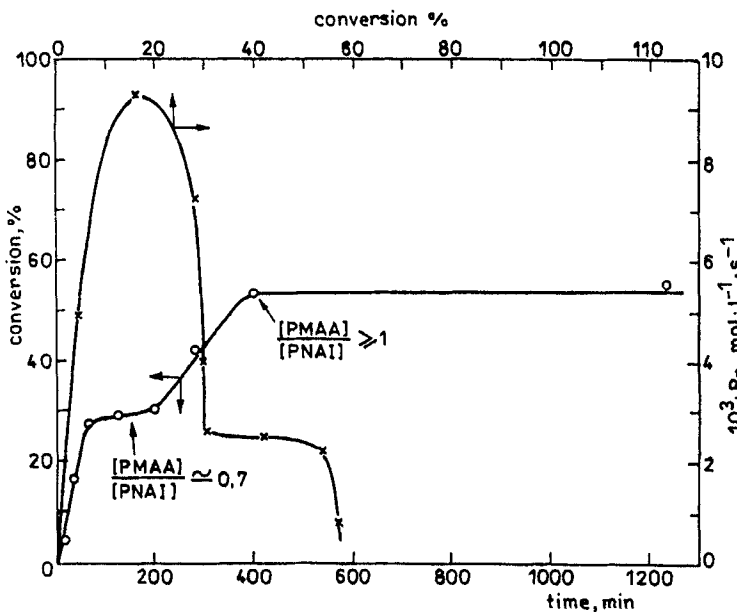A plot of the polymerization rate variation vs the $[PNAI]:[MAA]_0$ ratio presents an abnormal shape, with two maxima at $[PNAI]:[MAA]_0$ values of about 0.5

FIG. 8.   Conversion vs time and polymerization rate of methacrylic acid vs conversion curves ($[MAA]_0 = 1$ m, $[PNAI] = 1$ basemole$\cdot$L^{-1}, $[I_{20}] = 5 \times 10^{-2}$ m, $T = 70°$C).

and about 1.5. Similarly, the dependence of the polymerization rate on $[MAA]_0$ at a constant template concentration reveals a modification of the slope after a molar ratio of about 1:1 for the components of the system is reached (Fig. 6).

A jump in the ln $[\eta]$ can be observed around this value of the feed composition (Fig. 7). The evident control of the dimensions of the daughter polymer denotes that this is not a gel effect, presumably due to the increased viscosity of the medium, but a template effect, a consequence of the influence of matrix length and its association ability, for certain ratios, with the forming polymer.

The unusual behavior cannot be attributed only to the formation of complexes having different structures, depending on the feed composition, which seems to be characteristic for systems containing polyacids and polyethylenimine or its acylated derivatives [4, 5], because the conversion curve ($[MAA]_0:[PNAI] = 1$) also shows a two-stage increase (Fig. 8).

The composition of the products varies slightly with the monomer and template content in the feed and with the reaction time. It is obvious from elemental analysis and ^{1}H-NMR data that those with [PMAA]:[PNAI] ratios of 2:3 and 2:1 are preferred even for a large excess of MAA. These products appear to be the most stable complexes.
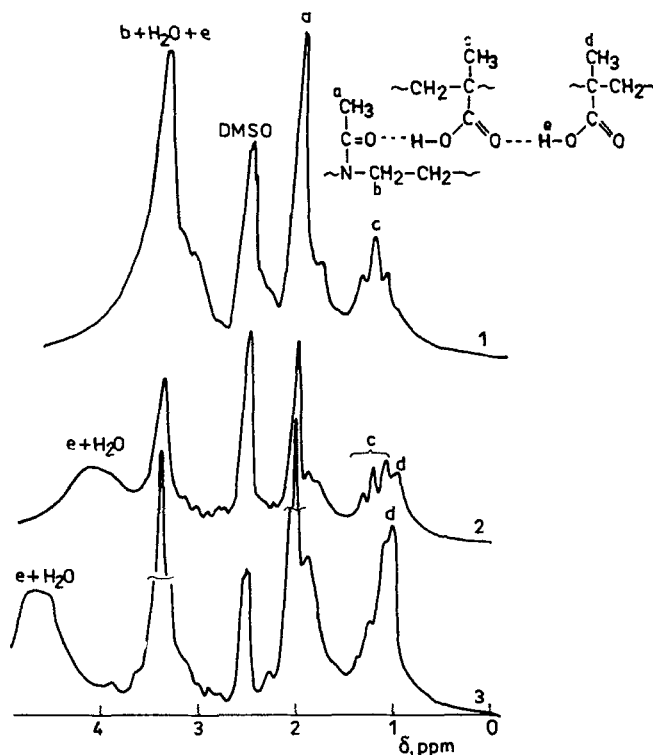

FIG. 9. ^{1}H-NMR spectra of the synthesized block copolymer (a) after 65 minutes, (b) after 1235 minutes, and (c) after 300 minutes from the beginning of polymerization. Polymerization conditions: (a, b) $[MAA]_0 = 1$ m, $[PNAI] = 1$ basemole·L^{-1}, $[I_{20}] = 5 \times 10^{-2}$ m; (c) $[MAA]_0 = 3$ m, $[PNAI] = 1$ basemole·L^{-1}, $[I_{20}] = 5 \times 10^{-2}$ m).

The strength of the interactions in the formed complexes resulted in splitting of the signal for the CH_3 group from the C_α of the PMAA sequences in the ^1H-NMR spectra, similar to PMMA (Fig. 9). This allowed us to distinguish between the different PMAA forms and thus to determine the tacticity of the PMAA blocks. It was found that the percent of isotacticity of the PMAA sequences decreased with time (i.e., from 24% at $t = 65$ hours to 10% at $t = 1235$ hours), thus favoring an increase of the percent syndiotacticity (respectively, from 23 to 34% during the same period of time). This suggests that the unusual two-stage polymerization might the consequence of replacement of the matrix during the process. In the first stages, PNAI is the template until its sites are practically all occupied. When the PNAI matrix is completely covered by the daughter chains, the last ones themselves become a matrix for the further polymerization of MAA (Fig. 9).

Following these considerations, the shape of the plot of the relative polymerization rate vs the initial template unit to monomer molar ratio [PNAI]:[MAA]$_0$ could be attributed to a two-step template polymerization, both stages proceeding according to a type I mechanism [2].

CONCLUSIONS

The radical polymerization of methacrylic acid in the presence of PNAI macroazoinitiators in aqueous solution was proved to yield water-insoluble products, identified as macromolecular complexes formed by H-bonding of the two component sequences of the synthesized block copolymers.

The characterization of the block copolymers and kinetic experiments revealed template features typical of a *zip* chain-growth mechanism with a maximum effect of template (PNAI) concentration on the polymerization rate at [PNAI]:[MAA]$_0$ = 0.5 and 1.5. The experimental data emphasize that a replacement of the matrix occurs during the polymerization process, i.e., following filling of the PNAI template sites. The generated daughter polymer is preferred as the new template. The replacement of the first matrix determines the modification of the molecular masses and the microstructure of the products.

Investigation of the photochemical polymerization of MAA in the presence of PNAI macroazoinitiators in very diluted aqueous solutions is in progress in order to study the influence of both templates on the tacticity of the daughter polymer.

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