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Confinement effects on the kinetics of formation of sequential semi-interpenetrating polymer networks

Yuri S. Lipatov, Tatiana T. Alekseeva (✉), Lyubov A. Sorochinskaya, Galina V. Dudarenko

Institute of Macromolecular Chemistry of NAS of Ukraine, Department of Physical Chemistry of Polymers, 02160 Kiev, Kharkovskoye Shausse 48, Ukraine

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Summary

Peculiarities of formation kinetics of sequential semi-interpenetrating polymer networks based on crosslinked polyurethane with different cross-linking density and linear polystyrene and polybutylmethacrylate have been studied. Polyurethane networks were synthesized differing in molecular mass M_c of the chains between cross-links. Monomeric styrene and butyl methacrylate were introduced into these networks by swelling them in monomers up to equilibrium. The kinetics of polymerization of monomers in swollen networks was investigated. The experimental data show the dependence of the kinetic parameters of polymerization on M_c, this dependence being different for various monomers. Sharp discrepancy in molecular mass distribution of polymers formed in various matrices has been observed. The differences in dependencies of reaction kinetics and molecular mass distribution are supposed to be connected to various dependence of the chain growth and termination of various monomers on the density of network, i.e. on the confinements imposed by the intranetwork space.

Introduction

During last years a great interest is declared to the behavior of polymeric molecules in confined state [1-3]. Some situations are considered: properties of thin films at the interface with solid, behavior of solutions and polymers in thin pores. In all these cases the polymeric molecules are situated in a very restricted space whose dimensions are comparable to the size of macromolecules [3-6]. Restrictions imposed by the small volumes on the behavior of polymeric molecules are very important. The static and dynamic properties of confined fluids are of interest in many fields because of their importance in a variety of technological processes, including catalysis, chromatography etc. A considerable progress in understanding the dynamic and thermodynamic properties of molecular liquids in restricted geometry has been made in recent years [1-9]. General agreement exists that properties of bulk liquids may change dramatically by confinement in small pores. The fluid in the pore is expected to have two distinct phases. The first one corresponds to the molecules in the inner pore volume and the other – to the surface-fluid interface. The behavior in the inner pore volumes may depend on such factors as the type of intermolecular interactions,

pore size and molecular mass of the molecules. Molecular properties of the interface primary depend on the surface forces, which can be attractive or repulsive depending on the polarity, adsorption energies and surface coverage [1, 2, 10, 11] The majority of experimental data indicate an increased viscosity reduction of self-diffusion and hindrance of reorientational motion in physisorbed molecular layers. Direct effect of the thickness of the thin surface layers on the glass temperatures was described as early as in 60-ties in some works [12-14]. There were published data on the effect of confinement on the peculiarities of the glass transition of macromolecules in interfacial layers for porous systems with two-dimensional spatial limitation (cylindrical pores of porous glass) [15, 16]. In spite of this, up to now there were no investigations of the confinement effect on the reactions of macromolecules formation. The systems where such an effect may be expected are sequential semi-interpenetrating polymer networks (semi-IPN). In such systems one of the components is synthesized in the pores of another network prepared preliminary. Such systems were widely investigated [17-21]. However the most of the works was dedicated to the study of the mechanical, viscoelastic, thermophysical and other physical properties of the material. The processes of the phase separation proceeding (if any) in sequential IPNs were also not investigated in spite of the great deal of works dedicated to such a processes in simultaneous IPNs [22]. For simultaneous IPNs the kinetics of the reaction of both components in the stating mixture was thoroughly studied [22]. At the same time, the kinetics of the reaction of the formation of the second linear or cross-linked polymers in first networks was almost not studied; there are no data about the effect of the confined space either on the reaction kinetics or molecular mass distribution of the second polymer formed. The only exception are two works [23, 24] where authors studied the kinetics of the polymerization of styrene and methyl methacrylate in beforehand prepared networks based on the methyl methacrylate copolymer with dimethacrylate tri-decaethyleneglycol and styrene with dimethacrylate ethylene glycol. It was found that growth rate constants by polymerization of styrene and methyl methacrylate in the network coincides with the corresponding constants by polymerization of the same monomers in bulk. The termination constant is lower as compared with bulk polymerization, which is the reason of the fast appearance of the gel effect. In the same works the peculiarities of the molecular mass distribution of linear polymers formed in networks were analyzed.
The aim of the present work was to establish the confinement effect on the reaction kinetics and molecular mass distribution of linear polymer formed in the matrix network of sequential semi-IPN. The peculiarity of this investigation consists of applying as a matrix of networks with various dimensions of the network cells, i.e. characterized by various values of M_c.

Experimental

Materials and synthesis

Semi-IPNs were produced by sequential method. 1st stage consisted of the synthesis of cross-linked polyurethane (PU) on the basis of poly (oxypropylene glycol) with molecular masses 500, 1000 and 2000 and triisocyanate adduct (2,4-2,6 tolulene diisocyanate and trimethylol propane). Reaction was performed at 60°C up to full conversion of the functional groups (monitored by IR-spectroscopy). The catalyst concentration (dibutyltin laurate) was $1.4 \cdot 10^{-4}$ mol/l. Synthesized products were dried under vacuum up to constant weight. On the second staged the second component was introduced into the network by swelling it in monomer (butylmethacrylate (BMA) and styrene (St)). Initiator of radical polymerization of monomers (2,2'-azo-*bis*-isobutyronitrile) was dissolved in monomers before swelling. The amount of monomer introduced into the network by swelling was dependent on the cross-linking density; the identical conditions of reaction in each case were supported. Polymerization was performed at 60°C to full exhausting of double bonds. The initiator concentration was taken $2.5\cdot10^{-2}$ and $5.0\cdot10^{-2}$ mol/l correspondingly for BMA and St. The amount of the second component in the network depends on the network density. In such a way semi-IPNs obtained using networks with different cross-linking density have various ratios of components. The amount of a monomer in the network was determined by the gravimetric method using the equation [25]:

$$\text{Component, \%} = [(m_{\text{IPN}} - m_{\text{PU}}) / m_{\text{IPN}}] \cdot 100,$$

where component % is the amount of the second component in semi-IPN, m_{IPN} and m_{PU} are the masses of the specimens of semi-IPN and matrix PU network. For each system the ratio of components in semi-IPN was estimated as an average value from 5 experiments (the measurement error no more 10 %).

Methods

To characterize matrix networks the molecular mass M_c of the chains between two junctions point was determined using Flory-Rehner method. As a solvent toluene was used. Values of the equilibrium swelling degree Q in toluene, M_c and effective network density ν_e/V for initial matrices are presented in Table 1.

The data on the equilibrium swelling degrees of matrices with different M_c in BMA (q_{BMA}) and styrene (q_{St}) were found from the equation [25]:

$$q,\% = [(m_{\text{swollen}} - m_0) / m_0] \cdot 100,$$

where m_{swollen} and m_0 are the masses of the swollen specimen and of initial one.

The kinetics of polymerization of monomers was studied at 60°C using differential calorimeter DAC-1-1A using the method described in detail in [26]. From the kinetic data the following parameters were determined: conversion of monomer at the onset of autoacceleration α_a, time of the onset of autoacceleration τ_a, maximum value of reduced reaction rate $W_{\max}$ of polymer formation and the time $\tau_{\max}$ of reaching $W_{\max}$. The reduced reaction rate of PBMA and PS formation calculated from $W_{\text{red}} = V/ [M]$, where $V = dM/dt$, M is the amount of monomer unreacted and t, the reaction time.

The linear polymers formed in matrices were extracted for the determination their molecular mass distribution (MMD). As an extragents were used ethylacetate for PBMA and toluene for PS. Extraction has been performed in Soxhlet extractor by boiling of corresponding solvent during 10-15 h.

The chromatographic investigation of extracted polymer has been done using liquid chromatograph "Du Pont" with application of a refractometric detector. The selection of the detector was determined by a fine visibility of PS and PBMA in a given spectra range. As an eluent has been used chloroform as a good solvent for both polymers. 5 % of methanol was added to exclude the adsorption interaction of PBMA, as a polar polymer, with active centers at silicagel surface. The analysis was performed using a bimodal column filled with silicagel "Zorbax". The calculation of the column calibration constants has been done using polystyrene standard "Du Pont" with molecular mass M_w = 233,000 and M_w/M_n = 1.01. Molecular characteristics were calculated on the basis of the program of “Insoftus”. The polymers amounts were taken in the limits not exceeding 150 mg and dissolved in 5 ml of eluent.

Results and Discussion

Table 1 shows the characteristics of PU networks, which served as a matrix for the formation of semi-IPN. The analysis of the data shows that for PU based on POPG 500 and 1000 the experimental values of M_c are lower compared with theoretical ones, whereas for POPG 2000 experimental values M_c are higher in comparison with theoretical values. These data correspond to the literature data for PU based on POPG of various molecular mass [27, 28]. The increasing density of cross-links for PU based on POPG 500 and 1000 may be explained by the formation of a network of strong physical (hydrogen) bonds, which contributes to the total network density. A more defective network is formed for PU based on POPG 2000. It is connected with low reactivity of end OH-bond of POPG 2000.

Table 2 presents the data on the values of equilibrium swelling of the matrix in starting monomers and the time of their attainment. Table 2 shows that the equilibrium swelling of PU networks in both monomers depends on the M_c of matrix, which determines various amount of monomers in matrices with different M_c, i.e. the component ratios in semi-IPNs (Table 3).

Table 1. M_c and effective cross-linking density of PU based on POPG with different MM

Sample	MM POPG	$K_p \cdot 10^4$, kg/mol·s	Q_t	M_c	$(\nu_e/V) \cdot 10^3$, mol/sm^3
PU-1	500	8.2	0.415	220	4.64
PU-2	1000	6.3	1.102	1170	0.96
PU-3	2000	5.1	2.800	5730	0.18

Table 2. The degree (q) and the time (τ) of equilibrium swelling of PU in BMA and styrene dependence on M_c of the network

Sample	$M_{c\ exp.}$	Buthylmethacrylate		Styrene	
		q, %	τ, min	q, %	τ, min
PU-1	220	15	150	32	120
PU-2	1170	70	134	93	75
PU-3	5730	186	110	257	65

Table 3. Kinetic parameters of initial PBMA, PS formation and in semi-IPNs

Sample	Ratio, %	τ_a, min	α_a	W_{max}, min^{-1}	τ_{max}, min
PBMA	–	101	0,33	0,026	174
PU-1/PBMA	87/13	144	0,02	0,055	338
PU-2/PBMA	59/41	91	0,03	0,072	217
PU-3/PBMA	35/65	25	0,05	0,090	140
PS	–	613	0,48	0,021	860
PU-1/PS	76/24	90	0,02	0,023	235
PU-2/PS	52/48	273	0,24	0,036	515
PU-3/PS	28/72	560	0,45	0,045	790

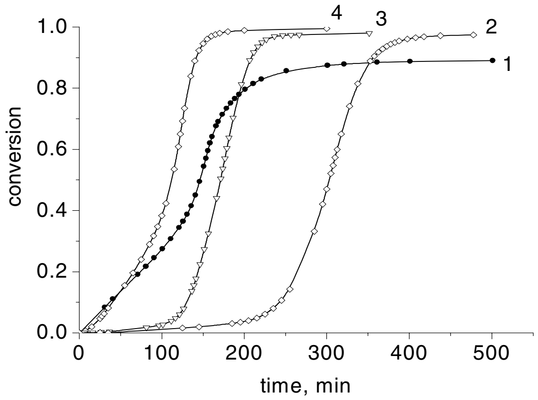

Figure 1. Kinetic curves of formation of initial PBMA (1) and PBMA in PU matrix: PU-500 (2), PU-1000 (3), PU-2000 (4)

Figure 1 shows the kinetic curves of the formation of pure PBMA (curve 1) and PBMA in matrix with different M_c. It is seen that conversion of BMA at the beginning of autoacceleration (α_a) is one order lower in comparison with polymerization of pure BMA, being insignificantly increased with increasing M_c (Figure 1, Table 3). The maximum value of reduced rate W_{red} for PBMA, growths with increasing M_c. Simultaneously, the time of attainment of maximum W_{red} diminishes from 340 min for PU-500 to 140 min for PU-2000 (Figure 2, Table 3).

As is known [29] in viscous media the role of diffusion processes in polymerization is very important. Diffusion may affect not only the chain termination but initiation reaction as well. Increasing viscosity of the media diminishes the constant of decomposition of the initiator and efficiency of initiation. The important role plays so called "cage" effects preventing the diffusion separation of a radical couple. It is probable, that by polymerization of BMA in PU-2000 diffusion limits only reaction of

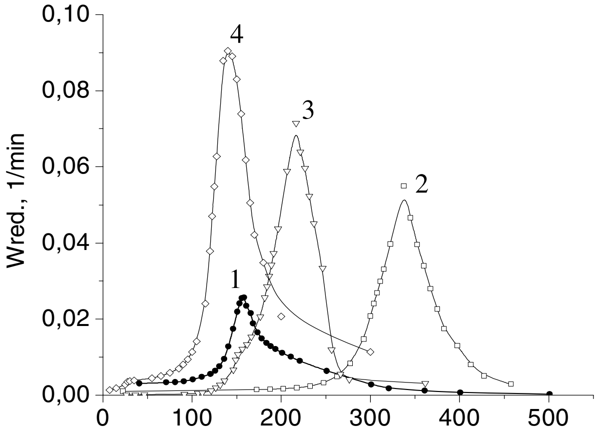

Figure 2. Dependences of reduced rate of polymerization W_{red} of initial PBMA (1) and PBMA in matrix on time: PU-500 (2), PU-1000 (3), PU-2000 (4)

chain termination. Really, maximum value of W_{red} for BMA polymerization increases three times as compared with polymerization of pure monomer. By polymerization of BMA in PU-500 the maximum of the time dependence of W_{red} broadens whereas the reaction rate diminishes. This effect may be related to essential decrease of the initiator decomposition rate and initiation efficiency. In this case the high density of the matrix network (4 times higher in comparison with theoretical one) impedes the outlet of radicals from the "cage" and diffusion may restrict not only the termination reaction but initiation. In [30] for polymerization of n-alkyl methacrylates it was shown that diminishing the termination constant is determined by lowering the free volume of the reaction media and by the appearance of topological entanglements leading to the formation of entanglement network. It was also established that by polymerization of styrene and MMA in beforehand prepared three-dimensional networks the termination constant is lower 3 orders as compared to bulk [23].

For styrene as the second component in semi-IPN the following regularities of the polymer formation in network cells were observed. From Figure 3 and Table 3 follows that styrene conversion at the point of autoacceleration and its time increase with increasing M_c (curves 2-4). Values of α_a and τ_a are lower in comparison with polymerization of free monomer. The same was observed for BMA polymerization. The maximum value of W_{red} with increasing M_c increases as well like in BMA case but maximum is shifted to lower reaction times as compared with free styrene as distinct from PBMA (Figure 4 and 2).

With diminishing M_c there is observed the lowering of styrene amount in semi-IPNs and diminishing of maximum W_{red}. The time of the onset of autoacceleration and time of attainment of maximum W_{red} for PS in PU-500 is essentially lower as compared with pure styrene and styrene in PU-1000 and PU-2000. For this case it may be supposed that by polymerization of styrene in PU-500 the rate constant of diffusion controlled termination reaction sharply decreases, which leads to the prompt beginning of autoacceleration (60 min) as compared with pure styrene (590 min) and for PS formation in PU-1000 and PU-2000 (Table 3). In given case by PS formation, diffusion controls only termination reaction.

In such a way for both monomers it is established that reaction kinetics strongly depends on the network characteristics, i.e. on the length of the chain segments

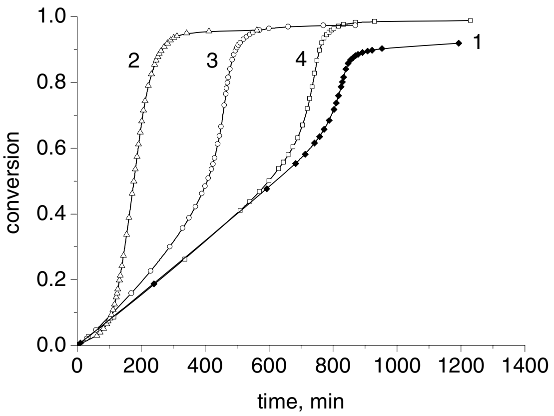

Figure 3. Kinetic curves of formation of initial PS (1) and PS in PU matrix: PU-500 (2), PU-1000 (3), PU-2000 (4)

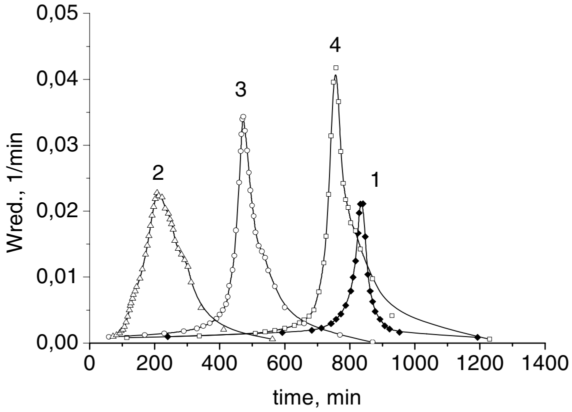

Figure 4. Dependences of reduced rate of polymerization W_{red} of initial PS (1) and PS in PU matrix on time: PU-500 (2), PU-1000 (3), PU-2000 (4)

between two junction points. This clearly confirms the effect of confinement on the reaction condition. At the same time there are interesting distinction between the behavior of BMA and styrene (Figure 2 and 4). In both cases the maximum value of reduced reaction rate W_{red} increases with M_c of the matrix. But for PBMA the time of attainment this maximum increases with diminishing M_c of the matrix, whereas for PS this time is increases with growthing M_c.

Let us now consider the data on molecular mass distribution (MMD) of linear polymers formed in various matrices. The main molecular characteristics M_w, M_n and M_w/M_n of extracted PBMA are given in Table 4 and Figure 5. MMD of PBMA, formed in matrices, changes with increasing M_c from 1.20 for PU-500 to 1.34 for PU-2000, whereas free PBMA has more broad distribution (2.2.). M_w of PBMA increases with growth of M_c, although M_w of free PBMA is much higher. This effect may be determined by that polymer chains formed under condition of hindered termination possess narrower MMD [31]. For PS the greatest M_w has the polymer formed in PU-500 and the lower – in PU-2000. M_w of pure PS is much higher (Table 4, Figure 6). With increasing M_c, MMD changes from 1.33 to 1.5, whereas for pure PS this characteristic has the value 2.07. Thus, PBMA with higher molecular mass is formed in matrices with the greatest M_c, whereas PS – in matrices with lower M_c.

Table 4. The data of extraction and molecular characteristics of linear polymers

Sample	Composition, %	The degree of the linear polymer extraction, %	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
PBMA	–	–	310	140	2,21
PU-1/PBMA	87/13	92,0	72	60	1,20
PU-2/PBMA	59/41	95,0	100	76	1,32
PU-3/PBMA	35/65	98,0	178	133	1,34
PS	–	-	290	140	2,07
PU-1/PS	76/24	86,0	186	140	1,33
PU-2/PS	52/48	94,0	165	137	1,20
PU-3/PS	28/72	98,0	150	100	1,50

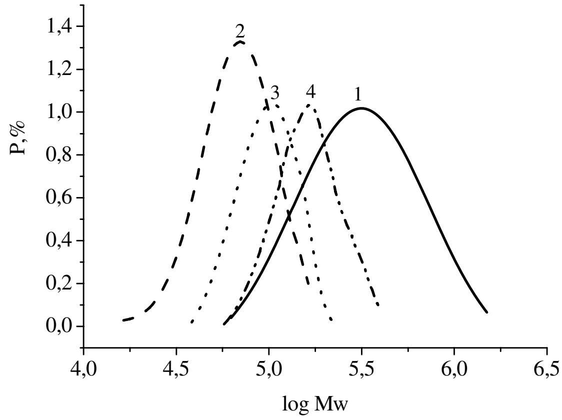

Figure 5. Molecular mass distribution for initial PBMA (1) and PBMA formed in PU matrix: PU-500 (2), PU-1000 (3), PU-2000 (4)

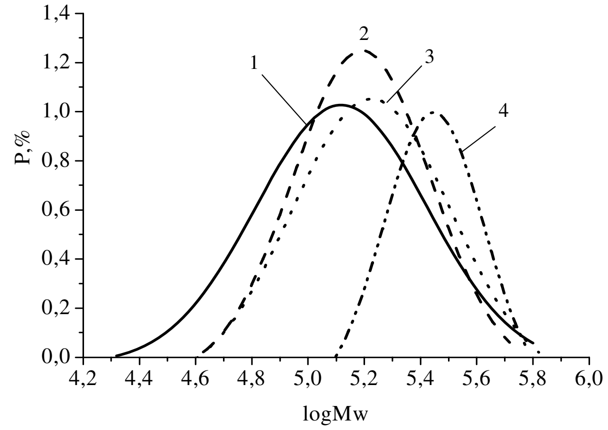

Figure 6. Molecular mass distribution for initial PS (1) and PS formed in PU matrix: PU-500 (2), PU-1000 (3), PU-2000 (4)

Conclusion

The experimental data confirm the expected dependence of the kinetics of polymerization of various monomers on the spatial restriction. The effect of confinement well known for physical properties of macromolecule reveals itself in the processes of macromolecules formation as well. For styrene polymerization the main kinetic parameters (α_a,τ_a and τ_{max}) depend in symbate way on the M_c, whereas for BMA polymerization there is direct correlation between α_a and M_c and reverse correlation between M_c and τ_a and τ_{max}.

We suppose that the differences in the reaction kinetics for both monomers and sharp discrepancy in MMD of polymers formed in various matrices are determined by the distinctions in the termination mechanism. It is known that by polymerization of butyl methacrylate the termination proceeds according to disproportionation whereas for styrene the recombination mechanism is operative. Probably, the conditions of termination in confined space depend on the termination mechanism. The differences in reaction kinetics may be also connected to various dependence of the chain growth and termination of various monomers on the density of network, i. e on the intranetwork space.

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