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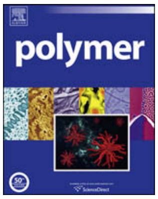

Photoinitiated polymerization in ionic liquids: Kinetics and viscosity effects

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ABSTRACT

The photo-induced polymerization of poly(ethylene glycol) dimethacrylate and poly(ethylene glycol) monomethacrylate (crosslinking and linear, resp.) in four imidazolium-based ionic liquids (ILs) containing the same cation or the same anion in pairs is reported. The kinetic studies were accompanied by detailed viscosity measurements, which showed the occurrence of an interesting phenomenon – a viscosity synergism in monomer/IL mixtures (i.e. the viscosity of the mixture is higher than the simple additive combination of viscosities of the two components). Viscosity synergism, very important for kinetic considerations, is especially strong for ILs of low viscosity and its magnitude depends on the monomer structure. The polymerization conducted in ILs was considerably faster than in a reference solvent. The propagation rate coefficients were influenced mainly by the anion structure whereas the termination rate coefficients by viscosity of the initial monomer/IL mixture (taking into account the synergistic effect). FTIR studies showed the existence of specific interactions between the carbonyl group in the monomer and C_2–H of the imidazolium ring; the polymerization rates were directly related to the magnitude of the monomer/IL interaction.

1. Introduction

The great popularity of ionic liquids (ILs) as solvents useful in many organic syntheses and chemical processes [1] made them interesting also for application as new solvents for polymerization reactions. Free radical, cationic, group transfer, coordination, electrochemical and step-growth polymerization in ionic liquid were investigated (Ref. [2] and references cited therein). ILs are generally viscous liquids with viscosities ranging typically from 10 to 500 mPa s at ambient temperature, which is comparable to viscosities of oils and two to three orders of magnitude higher than viscosities of traditional organic solvents [3]. The major advantage of using ionic liquids is their ability to dissolve a wide range of organic and ionic compounds to an appreciable extent, the negligible vapor pressure and high thermal and chemical stabilities. Additional interest results from the high polarity, high conductivity and a wide electrochemical window [4] potentially useful in electrochemical applications.

The number of papers devoted to radical polymerization in ILs is rather limited. Existing publications report on a significant enhancement in the polymerization rates and molecular weights and an increase in polymer yield as compared to conventional organic solvents or bulk [2,5–9] although lowering in molar masses and reduction of conversion were also observed [2,10,11].

Kinetic observations for a series of acrylate monomers proved that when the polymerization is carried out in ILs, propagation rate coefficients increase and this was related to increasing polarity of the medium which favors transition state involving charge transfer and/or complex formation between IL and either monomer or radical and results in lowering of activation energy [4–6,12]. On the other hand, termination rate coefficients decrease due mainly to high viscosity of ILs [4,12].

The majority of polymerizations in IL was conducted for difunctional monomers (containing one double bond, according to Flory's definition [13]), to find the influence of ILs both on the reaction rate and molecular weight of the polymer formed. In one report on polymerization of multifunctional (crosslinking) monomers in ILs, the latter served as porogenic solvents and to obtain IL–polymer composite resin suitable for evaluation in catalytic membranes [14].

A special case are ionic liquid monomers, containing both (meth)acrylate and IL moieties. Their polymerization rates were found to be highly dependent on the monomer structure, initial viscosity and, in some cases, on the presence of water [15,16].

Although free-radical polymerization in ILs is continuously a subject of investigations, there are only several reports on the photochemical initiation [15–19]. This type of initiation can be especially useful for preparation of solid polymer electrolytes by means of polymerization [17,19,20] due to the short reaction time

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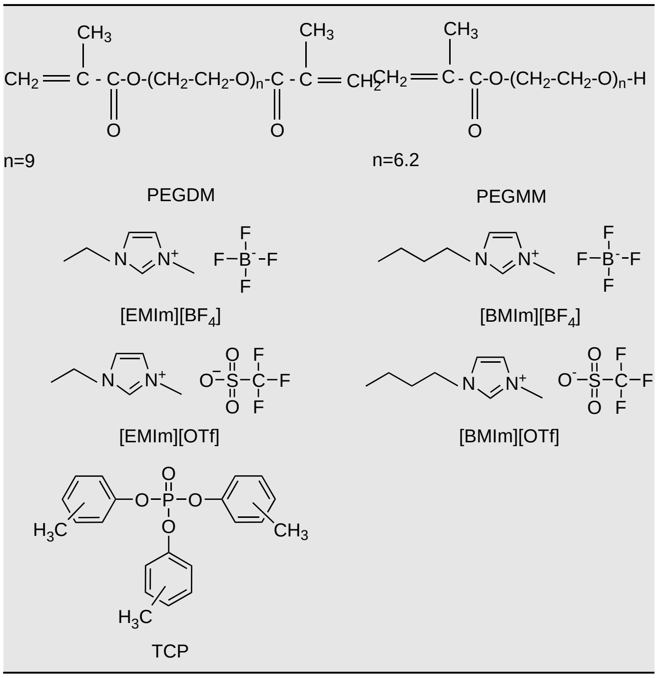
and ambient working temperature. We undertook detailed investigations in these two areas (photopolymerization kinetics and electrochemical applications) and got very good results using both crosslinking and linear monomers for preparation of solid polymer electrolytes [17,19,21].

This paper presents results of our investigations in the field of kinetics of photopolymerization in ILs. Because until now no attempt was made to compare the influence of individual anions and cations on the monomer/IL mixture properties, interactions and polymerization rate coefficients, we undertook research in this subject for two analogous monomers: tetrafunctional poly(ethylene glycol) dimethacrylate (PEGDM) and difunctional poly(ethylene glycol) monomethacrylate (PEGMM), forming crosslinked and linear polymers, resp. Four ionic liquids selected for the investigations 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF_4]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]), 1-ethyl-3-methylimidazolium trifluorome thanesulfonate ([EMIm][OTf]) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIm][OTf]) contained the same cation or the same anion in pairs, which could enable to find the effect of the cation and anion structure on the polymerization rate and propagation and termination rate coefficients. Analogous polymerizations in bulk and in a molecular diluent of medium polarity, tricresyl phosphate (TCP) (which viscosity is very close to viscosities of two of the ILs used, see Table 1), served as references.



2. Experimental

PEGDM, PEGMM and TCP were delivered by Aldrich; the monomers were purified by column chromatography before use and were stored over molecular sieves. All the ILs, delivered by Merck, were of high purity (≥99.0%; water content ≤ 100 ppm; halide content ≤ 100 ppm).

Reaction rates (R_p) and conversions (p) were determined by differential scanning calorimetry (DSC) under isothermal conditions at 40 ± 0.01 °C in a high-purity argon atmosphere (<0.0005% of O_2) using the Pyris 6 instrument (Perkin–Elmer) equipped with a lid especially designed for photochemical measurements. The 2-mg samples were polymerized in open aluminum pans with the diameter of 6.6 mm. The polymerizations were initiated by the light from a medium pressure mercury lamp (glass filter 366 nm, light intensity 2.75 mW cm^{-2}). As the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Ciba) with concentration 1 wt.-% was used. All DSC photopolymerization experiments were conducted at least in triplicate. The reproducibility of the results was about ±3%. For computations, the heat of polymerization was taken to be 56 kJ mol^{-1} per one double bond [22].

The experimental data for calculations of the polymerization rate coefficients were obtained from postpolymerization processes, which were registered after stopping the irradiation at various degrees of double bond conversion. The decrease of the reaction rate over 10 s reaction time after the light was removed was used to determine propagation (k_p) and bimolecular termination (k_t^b) rate coefficients. The coefficients were calculated according to the bimolecular termination model [23] from the following equations:

$$\frac{[M]_t}{(R_p)_t} = \frac{2 \cdot k_t^b}{k_p} \cdot t + \frac{[M]_0}{(R_p)_0} \tag{1}$$

$$(R_p)_0 = \frac{k_p}{\left(k_t^b\right)^{0.5}} \cdot [M]_0 \cdot (\phi \cdot I_a)^{0.5} \tag{2}$$

where $(R_p)_t$ and $[M]_t$ are the polymerization rate and double bond concentration at time t of the dark reaction, resp., and $(R_p)_0$ and $[M]_0$ are the parameters at the moment of breaking the irradiation, ϕ denotes quantum yield of initiation and I_a intensity of the light absorbed.

The rate coefficients were calculated in the form of k_pF and k_t^bF, where $F = (\phi I_a)^{0.5}$, F was assumed to be constant in the range of conversions studied.

The viscosities of the investigated compounds at the polymerization temperature, η^{40}, were measured by a Brookfield Digital Viscometer model DV-II at the shear rate 10–160 rpm (no dependence on the share rate was observed). IR spectra were recorded as thin films between KBr windows on Nexus Nicolet model 5700 FTIR spectrometer.

Theoretical viscosities of the monomer/solvent binary mixtures were calculated from equation (3) [24,25]:

$$\ln \eta_{mix} = \sum_{i=1}^{2} x_i \ln \eta_i \tag{3}$$

and excess logarithm viscosities $(\ln \eta)^E$ from equation (4) [26]:

$$(\ln \eta)^E = \ln \eta_{mix} - \sum_{i=1}^{2} x_i \ln \eta_i \tag{4}$$

where η_{mix} refers to the mixture viscosity, x_i are mole fractions and η_i are individual component viscosities.

Table 1
Viscosities of the monomers, ionic liquids and TCP at 40 °C.

Compound	PEGDM	PEGMM	[EMIm][BF_4]	[BMIm][BF_4]	[EMIm][OTf]	[BMIm][OTf]	TCP
Viscosity, mPa s	20.4	20.0	24.7	46.8	22.7	43.5	23.3

Diffusion rate coefficients k_{diff} were calculated from the well-known relation:

$$k_{diff} = \frac{8000 \cdot R \cdot T}{3 \cdot \eta} \tag{5}$$

where k_{diff} is expressed in [$\mathrm{dm^3\,mol^{-1}\,s^{-1}}$], R is gas constant [$\mathrm{J\,mol^{-1}\,K^{-1}}$], T is temperature [K], and η is system viscosity [Pa s].

3. Results and discussion

The problem associated with the investigation of polymerization processes in ILs is the limited solubility of the monomers and resulting polymers. PEGDM is well soluble in all the selected ILs, however, PEGMM is not well soluble in [BMIm][BF_4] (no reproducible results were obtained), thus, in this one case the viscosity and polymerization kinetic measurements could not be made. On the other hand, its linear polymer, poly-PEGMM, is compatible with the remaining ILs used even at 70% concentration of the latter (no visible phase separation occurs), whereas the crosslinked polymer (poly-PEGDM) is compatible only with [EMIm][OTf] and [BMIm][OTf]. Mixtures of poly-PEGDM with the two ILs containing [BF_4]$^-$ anion show a phase separation (reaction mixture becomes cloudy), stronger in [EMIm][BF_4] (beginning from about 9% of double bond conversion) and a partial in [BMIm][BF_4] (beginning from about 20% of double bond conversion).

If the increased polarity of the medium is the factor increasing the propagation rate coefficient, we should take it into account when comparing the effects of ILs' structure on the photopolymerization rate. Although there is no clear rule for the correlation between the polarity and IL structure, there are some indications that the polarity correlates with anion size, i.e. effective charge density. Thus, the ILs containing [BF_4]$^-$ anion are more polar than those containing [OTf]$^-$ anion [27]. On the other hand, an increase in the length of the alkyl chain results in a reduction of micropolarity of the IL [28].

The initial viscosity of a polymerizable composition is an important factor influencing the termination rate coefficient (an inverse proportionality). Thus, judging from the values of viscosities shown in Table 1 we could expect a small and similar effect of [EMIm][BF_4], [EMIm][OTf] and TCP on k_t^b (all of them show very similar viscosities, close to viscosities of the monomers) and an observable and similar effect of [BMIm][BF_4] and [BMIm][OTf]. It is worth to note that whereas the anion structure is responsible for the polarity of the IL [27], the viscosity of the 1,3 alkyl-methyl disubstituted imidazolium-based ILs is determined by the alkyl substituent (Table 1) (in agreement with Ref. [2]), and, to a much lesser degree, by the anion type.

3.1. Photopolymerization rates

The kinetics were followed for systems containing 50 wt.-% and 70 wt.-% of ILs. The rates of the photopolymerization in bulk, in ILs and in TCP as functions of the irradiation time t and double bond conversion p are shown in Figs. 1 and 2.

Fig. 1 presents the results obtained for the crosslinking monomer in which polymerization occurs with immediate gel effect. Dilution of the monomer usually decreases the maximum polymerization rate $R_p^{\max}$ due to the decrease in double bond concentration, thus, a significant reduction of $R_p^{\max}$ is observed in TCP. The addition of ILs accelerates the polymerization and markedly

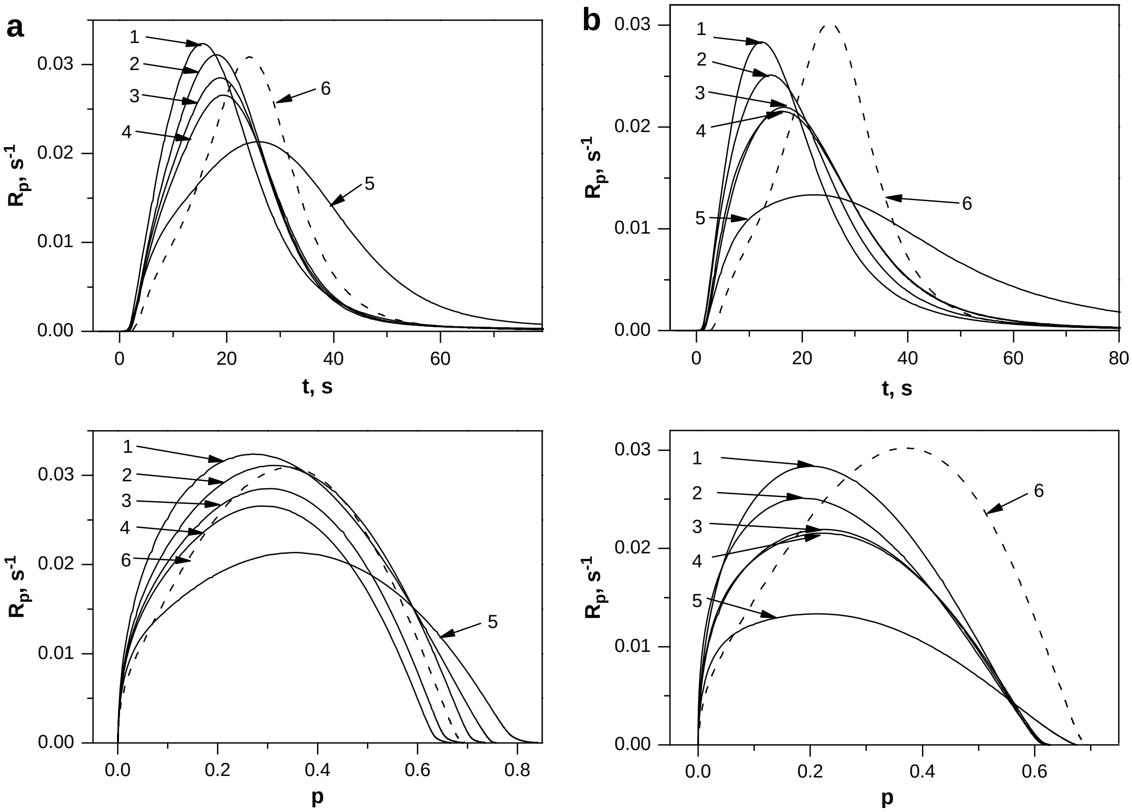


Fig. 1. Polymerization rate R_p at 40 °C as a function of the irradiation time t and the double bond conversion p for PEGDM photopolymerization in 1 –[EMIm][BF_4], 2 – [BMIm][BF_4], 3 – [EMIm][OTf], 4 – [BMIm][OTf], 5 – TCP, 6 – bulk. IL content: a) 50 wt.-%; b) 70 wt.-%.

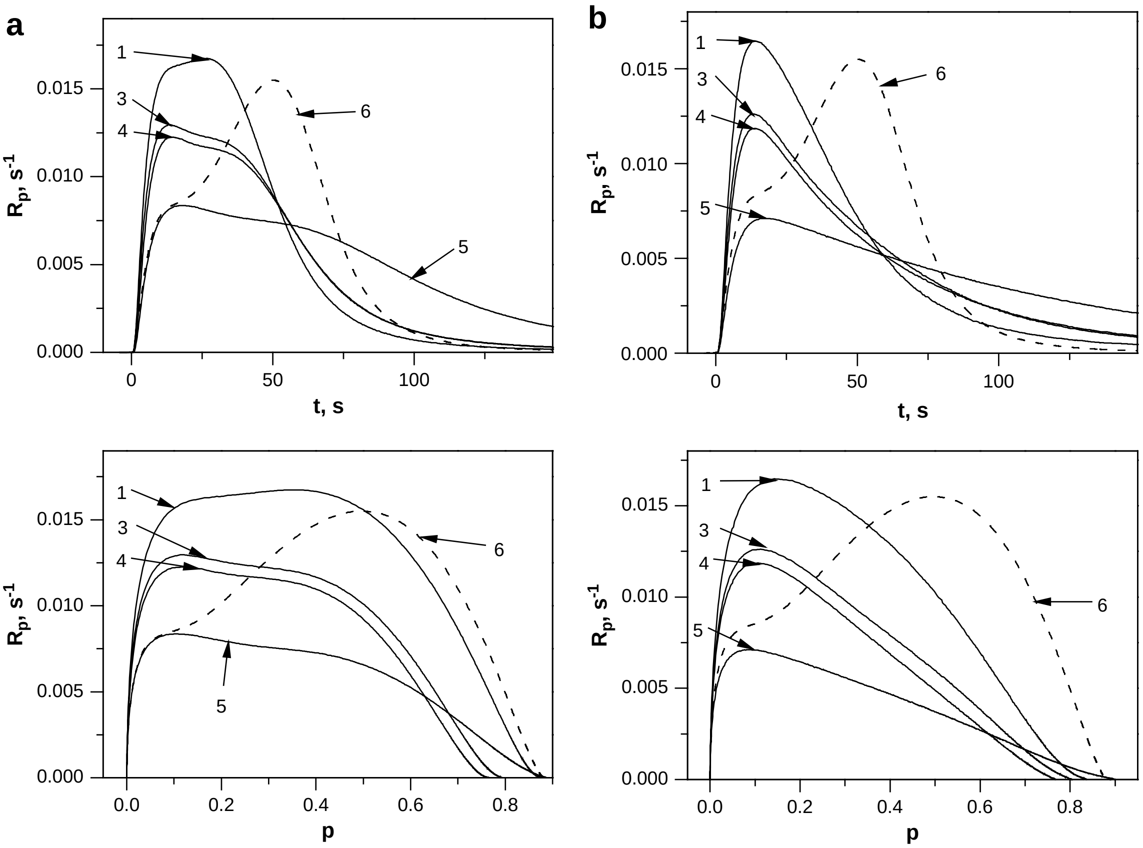


Fig. 2. Polymerization rate R_p at 40 °C as a function of the irradiation time t and the double bond conversion p for PEGMM photopolymerization; IL content: a) 50 wt.-%; b) 70 wt.-%. Description of curves as in Fig. 1.

increases R_p^{max} in comparing to the polymerization in the reference solvent. At 50% monomer concentration in ILs containing $[BF_4]^-$ anion the polymerization occurs even faster than in the bulk. Further increase in IL concentration to 70 wt.-% results in lower polymerization rates than in bulk. The latter decreases in the order: $[EMIm][BF_4] > [BMIm][BF_4] > [EMIm][OTf] > [BMIm][OTf]$ indicating that the rate enhancement is stronger in ILs containing $[BF_4]^-$ anion and rather $[EMIm]^+$ cation. Such a result seems to confirm the supposition that the polarity of ILs is the main factor influencing the polymerization rate [4,12] and dominates over the effect of system viscosity. A complicating factor is the phase separation occurring in ILs containing $[BF_4]^-$ anion, which can prolong the life-time of the propagating radicals linked to the precipitated polymer and increase in this way the k_p/k_t^b ratio [4]. The final double bond conversion, which is restricted by the system mobility, is only slightly influenced by ILs. Somewhat surprising result is the high double conversion in TCP, which may be associated with its plasticizing effect.

Qualitatively similar results were obtained for PEGMM (Fig. 2). This monomer forms a linear polymer and the gel effect starts at about 15% of double bond conversion. Dilution of the monomer by 50 wt.-% of the solvent reduces the gel effect significantly and causes its complete disappearance when the solvent concentration reaches 70 wt.-%. When the polymerization is carried out in ILs, the reaction rates are much higher than in bulk (before the gel effect) and than in the reference solvent. The activity of ILs in acceleration of the polymerization is the same as in the case of PEGDM, but the kinetic picture is not perturbed by visible phase separation.

3.2. Viscosity of monomer/IL system

As was indicated, the knowledge of the viscosity of ILs is of prime importance from an engineering point of view as it plays a major role in many industrial transport operations and affects so important property such as diffusion [3]. However, for practical applications more important seems to be the viscosity of the entire IL-containing reacting system. Generally, the viscosity of ILs after addition of cosolvents or water decreases [3,30–34]. It was reported earlier [28] that the viscosity of a mixture of an imidazolium salt and butyl methacrylate is lower than the viscosity of the pure IL due to the low viscosity of the monomer. Because the initial viscosity (along with that growing during the polymerization) is the main factor influencing the termination rate, we paid a special attention to the viscosity of PEGDM/IL and PEGMM/IL systems. The initial viscosities were measured as a function of IL concentration and the results are shown in Figs. 3a and 4a. The figures present also the theoretical viscosities of the monomer/IL mixtures calculated from equation (3).

The results obtained are surprising: the mixtures of both the monomers with ILs show markedly higher viscosities than the individual components. The relative increase in viscosity is the higher; the lower is IL viscosity. The only exception is [BMIm][OTf] with PEGMM, but even in this case a substantial deviations from the calculated values can be observed.

If two liquids have greatly different particle interactions, as in our case, the viscosity of the mixture may be greater or lesser than either of the two liquids. This phenomenon can be described by the excess logarithm viscosity $(\ln \eta)^E$, defined by equation (4). As can be seen in

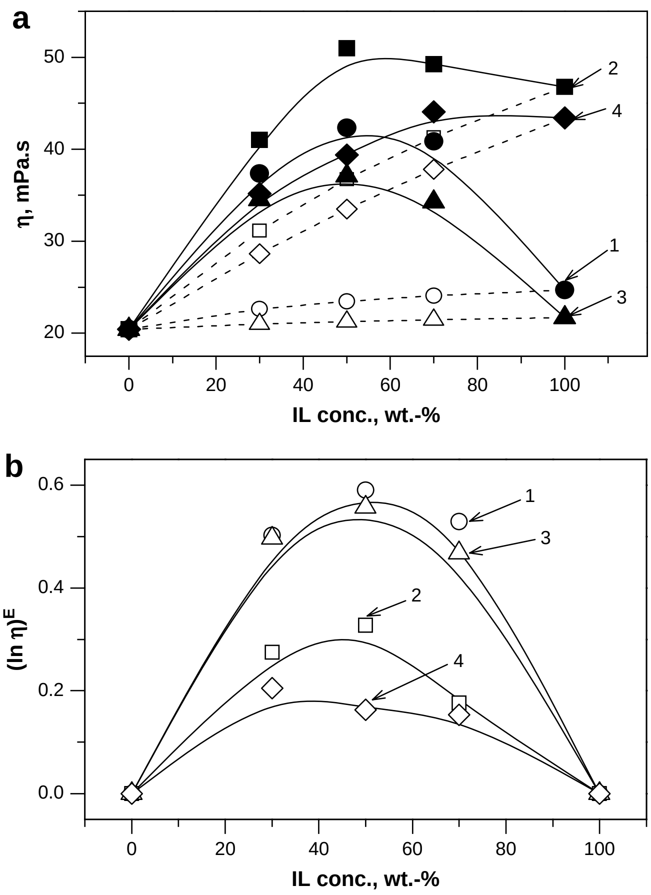


Fig. 3. (a) Viscosity of the PEGDM/IL mixtures: measured (filled symbols) and calculated (open symbols) and (b) excess logarithm viscosity as a function of IL concentration at 40 °C. Description of curves as in Fig. 1.

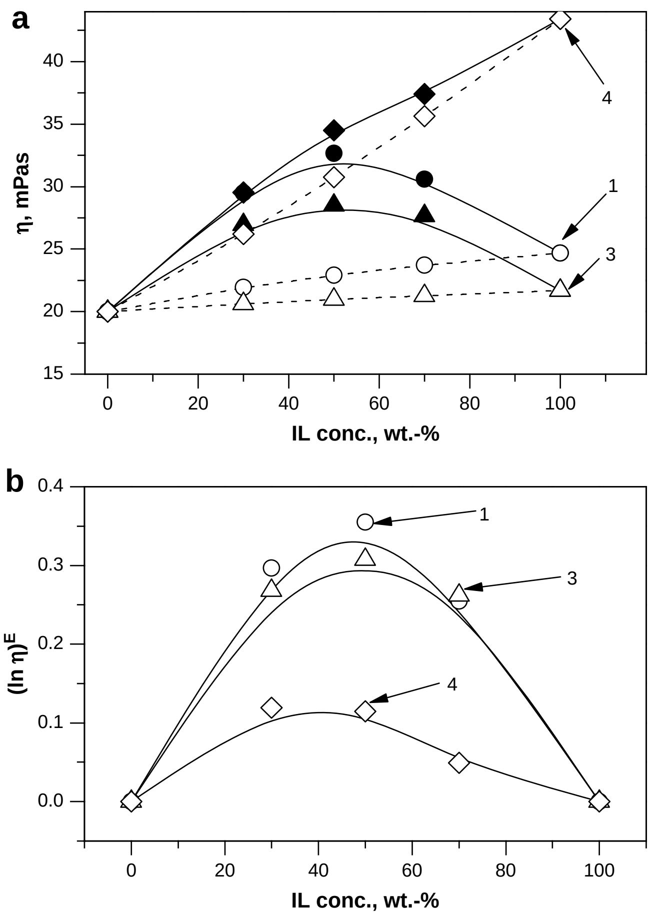


Fig. 4. (a) Viscosity of the PEGMM/IL mixtures: measured (filled symbols) and calculated (open symbols) and (b) excess logarithm viscosity as a function of IL concentration at 40 °C. Description of curves as in Fig. 1.

Figs. 3b and 4b showing (ln η)^E values, the deviations are positive and significant. This indicates on strong specific interactions between the ILs and monomer molecules, the greatest at 1:1 weight ratio. One can speculate that strong coulomb interaction between the ions in ILs is weakened upon mixing with the monomer [26] and monomer/IL interactions appear (between the monomer carbonyl group and the protons of the imidazolium ring (mainly at C2) [29]), which increases the cohesive forces [30]. These factors may be the reason for the observed increase in viscosity. It is possible that also the oxygen atoms in oxyethylene units can play a role.

The strong viscosity synergism (meant as an effect of the interaction of the actions of two agents such that the result of the combined action is greater than expected as a simple additive combination of the two agents acting separately) in the case of ILs of lower viscosity (mainly [EMIm][BF$_4$] and [EMIm][OTf]) (Figs. 3a and 4a) can suggest also that the interactions between these ILs and the monomers studied are stronger than between the molecules of the neat ILs. In the case of butyl-containing ILs the longer substituent increases van der Waals interactions leading to higher viscosities. Thus, the increase in viscosity resulting from interactions between the monomer carbonyl group and the imidazolium ring becomes relatively smaller.

Despite that the viscosities of the two investigated monomers are very close, the viscosities of their mixtures with ILs differ and are markedly higher in the case of the tetrafunctional monomer. As a result, the viscosity deviations for the PEGDM/IL mixtures (Fig. 3b) are almost twice higher than those for PEGMM/IL mixtures (Fig. 4b). This points to stronger intermolecular interactions between ILs and PEGDM than PEGMM molecules, which may result from the fact that PEGDM molecule contains two carbonyl groups vs. one in PEGMM. The stronger interactions in (and higher viscosities of) PEGDM-containing mixtures suggest in turn that the influence of the initial viscosity on the photopolymerization of this monomer in ILs should be stronger in comparing to PEGMM.

Especially interesting is that the highest and similar deviations ((ln η)^E values) were found for ILs containing ethyl-substituted imidazolium ring ([EMIm][BF$_4$] and [EMIm][OTf]). With the same cation, the values of (ln η)^E are somewhat higher for ILs containing [BF$_4$]$^-$ anion. These observations seem to confirm the supposition that the increase in viscosity is mainly related to interactions involving protons of the imidazolium ring, because the H-bond acidity is determined by the cation structure, although it is also modulated by the anion [27].

To the best of our knowledge, our work is the first report on the strong synergism in viscosity of IL/organic solvent (in this case monomer) mixture. No synergism was observed for monomer/TCP system; the dependence $\eta = f$(TCP conc.) was practically linear.

The initial assumption on classification of the monomer/solvent mixtures to groups of expected lower viscosity (with [EMIm][BF$_4$], [EMIm][OTf] and TCP) and higher viscosity (with [BMIm][BF$_4$] and [BMIm][OTf]) was not confirmed by the experimental data (see Figs. 3a and 4a). Thus, simple correlations “the higher viscosity of the IL used, the lower k_t^b value” or “the higher IL concentration, the higher viscosity of the reaction mixture” used sometimes in the lit. (e.g. [34]) may not be necessarily correct. For kinetic studies, it is

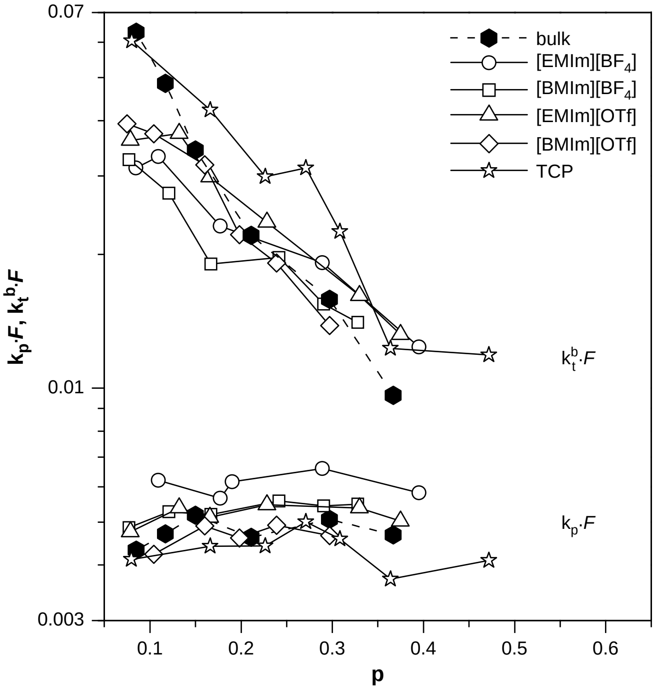


Fig. 5. Parameters related to propagation (k_pF) and termination (k_t^bF) rate coefficients as a function of double bond conversion for the polymerization in solvents and in bulk. Monomer: PEGDM, solvent conc.: 50 wt.-%.

necessary to measure the viscosity in the whole range of compositions investigated.

3.3. Polymerization rate coefficients

The propagation and termination rate coefficients (in the form of k_pF and k_t^bF) were estimated at the 50 wt.-% content of ILs, at which the differences in viscosities of the monomer/IL systems are the highest. These parameters were expected only to find the trend followed by true k_p and k_t^b coefficients with changing the cation or anion structure.

Determination of rate coefficients as the product with quantum efficiency of initiation gives rise to a question whether the quantum efficiency remains the same in all the ILs used. The initiation quantum yield is in turn a product of dissociation quantum yield Φ_{diss} (0.95 for DMPA) and probability of the reaction of the initiating radical with the monomer p_{RM} [35]. DMPA has short triplet states and the monomer quenching is not a competitive reaction to its cleavage; thus Φ_{diss} can be considered as mostly independent of the media [35], and we may expect the same for ILs. Probability p_{RM} depends mainly on the addition rate constant of primary radicals to the monomer k_i and on side reactions (the latter in ILs are yet unknown). The k_i value must be modified when the addition of primary radicals to the monomer molecule is diffusion controlled, i.e. when the diffusion rate constant k_{diff} is lower than the addition rate constant. DMPA photodissociation gives benzoyl, dimethoxybenzyl and methyl radicals. Benzoyl radical reacts at relatively low rate constant with methacrylates ($\sim 10^5\ M^{1\ -}s^{-1}$) and addition rate constants of dimethoxybenzyl and methyl radicals are even lower [35]. In our case diffusion rate constants in 50% monomer solutions varied from about 10^8 (in ILs) to about $3\times10^8\ dm^3\ mol^{-1}\ s^{-1}$ (in TCP and in monomers). This means that at the beginning of the polymerization the initiation is not diffusion controlled and the quantum yield of initiation should be similar in all the compositions studied (if strong and different specific interactions between the radical and ILs do not occur).

The estimated polymerization rate parameters are shown in Fig. 5 (for PEGDM) and Fig. 6 (for PEGMM) as a function of conversion. Considering the propagation rate coefficients one can see that although the plots are rather close to each other and there is a large scatter of data, generally k_p increases in IL whereas in TCP decreases in comparing to bulk polymerization. The order of decreasing k_p values corresponds to the order of decreasing values of the polymerization rates for the both monomers. This suggests that the k_p values are dependent on the anion structure, which in turn is mainly responsible for IL polarity; such a conclusion is in agreement with Ref. [5].

Although the k_p values seems to be similar for the two monomers (with slightly lower k_pF value for PEGMM), the k_t^b values are markedly lower for the crosslinking monomer due to the effect of network formation, which limits diffusion of macroradical chain ends from the early polymerization stages.

Both for PEGDM and PEGMM the highest k_t^b values were obtained for systems of lowest viscosity – the ones containing TCP (21.9 and 21.1 mPa s, resp.). This, together with the lowest k_p values, is responsible for the lowest polymerization rates in TCP. In the case of PEGMM/IL mixtures the $k_t^b = f(p)$ curves almost coincide, in contrast to those in PEGDM/IL mixtures, which can result from earlier mentioned greater viscosity effect in the latter. For PEGDM/IL system, where the $k_t^b = f(p)$ curves are separated, one can observe that the order of increasing k_t^b values corresponds to the order of decreasing initial η values of the monomer/IL mixture in 1:1 weight ratio, at least at low conversions, until the polymerization occurs in the homogeneous system. However, this dependence may be complicated by phase separation, which lowers the viscosity of the polymerizing medium. This factor may be one of the reasons for the unclear situation at medium conversions.

Generally, the polymerization rates in ILs (at 10% of conversion) are higher than in TCP about 1.3–1.9 times and this increase is somewhat higher than the increase in k_p (about 1.1–1.6 times). On the other hand, the k_t^b values in ILs are lower than in TCP by a factor

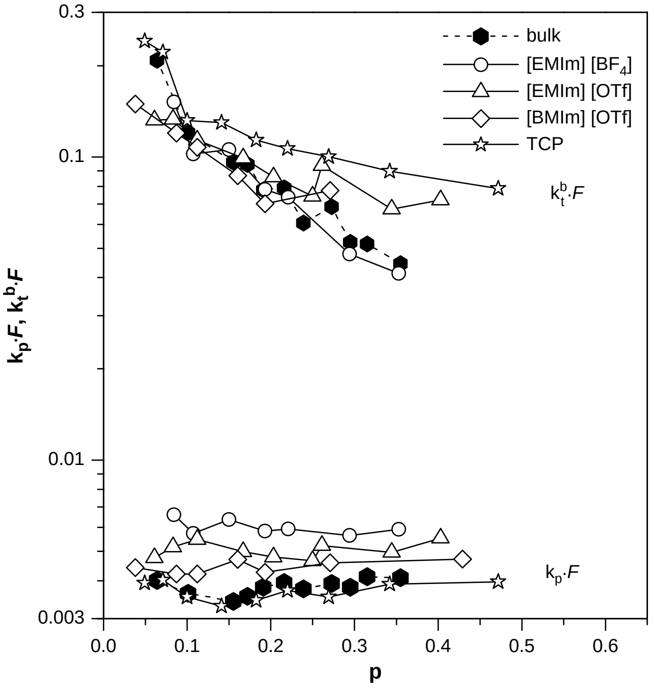


Fig. 6. Parameters related to propagation (k_pF) and termination (k_t^bF) rate coefficients as a function of double bond conversion for the polymerization in solvents and in bulk. Monomer: PEGMM, solvent conc.: 50 wt.-%.

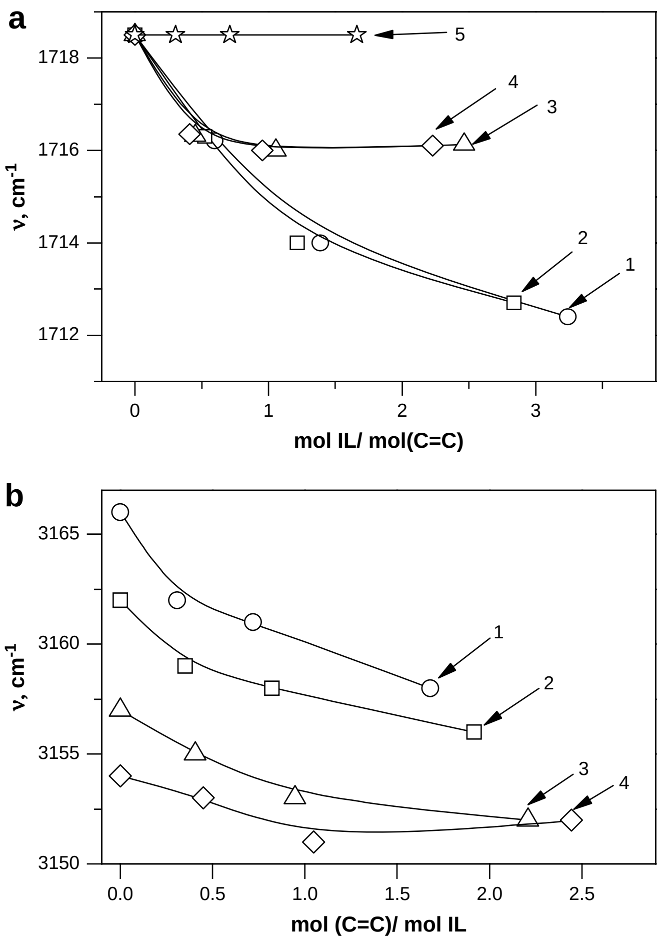


Fig. 7. Peak maximum positions: (a) ν_{max}(C=O) in the monomer and (b) ν_{max}(C_2–H) in IL, as a function of composition of PEGMM/solvent mixture. Description of curves as in Fig. 1.

of 1.25–1.68, which increases the polymerization rate by a factor of 1.1–1.3 (inverse square root dependence), i.e. to similar or somewhat lesser degree than the acceleration resulting from the increase in k_p (direct proportionality). Harrison et al. [12] observed twofold increase in k_p of methyl methacrylate (MMA) in 50% v/v IL solution both at 25 and 40 °C (relative to bulk MMA), which is not far from our results. On the other hand, k_t^b in work [12] was at 25 °C about 10 times lower than in bulk. Such strong reduction of k_t^b results from very large difference between the viscosity of the monomer and the IL (1-butyl-3-methylimidazolium hexafluorophosphate) used. According to data presented in Ref. [12], the 50% solution was about 10 times more viscous than the neat monomer, which leads to about triple increase in the polymerization rate. Thus, in the system described in the paper discussed, the accelerating effect resulting from the reduction of the termination rate outweighed that resulting from the increase in propagation rate, whereas in our case the accelerating effect associated with the increase in the propagation rate seems to be slightly higher.

Theoretically possible is also a case, when IL viscosity (and the viscosity of the monomer/IL mixture) will be so high that the viscosity will become the main determining factor both for k_t^b and k_p (as was observed for some ionic liquid monomers [16]).

3.4. Spectroscopic investigations

In imidazolium-based ILs cation–anion interactions are controlled by the anion, whereas the C_2–H of imidazolium loosely

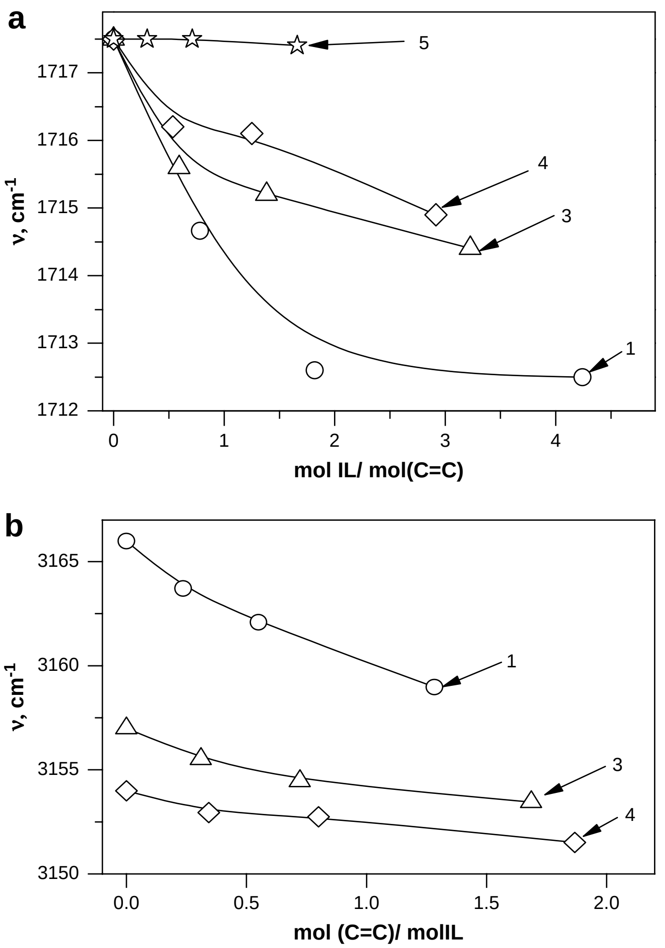


Fig. 8. Peak maximum positions: (a) ν_{max}(C=O) in the monomer and (b) ν_{max}(C_2–H) in the IL, as a function of composition of PEGMM/solvent mixture. Description of curves as in Fig. 1.

interacts with its counterion, but can readily interact with an H-bonding acceptable solute [29]. Thus, if there is any interaction between the monomer carbonyl group and C_2–H of the imidazolium ring, we should observe a shift of the IR absorption peaks of these two groups. Moreover, the position of the carbonyl group absorption may indicate relative strengths of polar interactions [5].

The influence of increasing amounts of ILs (expressed as the number of IL molecules per one methacrylate function) on the PEGDM and PEGMM carbonyl stretching is presented in Figs. 7a and 8a. The position of the carbonyl peak does not change in the presence of TCP, whereas a marked shift to lower frequencies is observed in the presence of ILs. The size of the shift excludes rather classical hydrogen bonding, the more so no bimodality of the peaks appeared (in agreement with Ref. [5], Fig. 9).

It is interesting that increasing IL content up to the equimolar ratio with respect to the monomer molecule causes much faster shift of ν_{max}(C=O) position than at higher IL concentration. The shifts are much greater in ILs containing $[BF_4]^-$ anion. This may suggest that the carbonyl group is sensitive mainly to the IL polarity determined by the anion type.

The frequency of C_2–H absorption [36,37] shown in Figs. 7b and 8b (at "0" on x-axis) varies with the IL structure; it decreases in the order [EMIm][BF_4] > [BMIm][BF_4] > [EMIm][OTf] > [BMIm][OTf]. This order corresponds to the strength of interactions between the cation and the anion; such interactions are stronger in the case of a smaller anion [29]. Moreover, the analogous order reflects

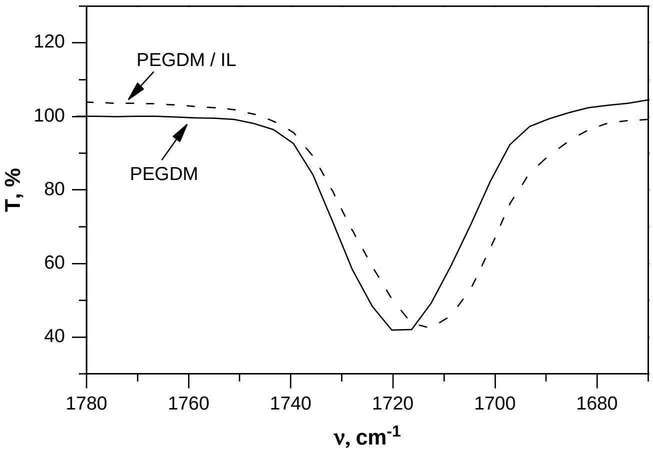


Fig. 9. IR spectra of PEGDM and its mixture with 70 wt.-% of [EMIm][BF_4].

also the accelerating activity of the ILs. This leads to the conclusion that the polymerization rate is the higher; the stronger is the cation–anion interaction in the IL. The interaction with the monomer is demonstrated by a shift to lower frequencies when the number of double bonds per IL molecule increases. The magnitude of the shift of $\nu_{max}(C_2\text{–}H)$ reflecting the strength of the monomer/IL interactions decreases in the same order as given above, which again correlates well with the activity of ILs in acceleration of the polymerization. One may speculate that monomer/IL interactions may lead to the formation of associates ("locally ordered structures" [2]), which favor the polymerization.

4. Conclusion

The results presented in this work indicate that the influence of ILs on the polymerization of methacrylate monomers is complex. One of the key factors seems to be system viscosity. Interactions of monomers with ILs can lead to unexpected increase in viscosity resulting from viscosity synergism, which is important both for kinetic measurements and practical applications. However, not all monomers show this effect (judging from the lack of reports and our further work, which is in progress) but its existence makes viscosity measurements of the monomer/IL system especially important when the polymerization kinetics are considered. Our results showed that at the beginning of the polymerization the k_t^b values were strongly correlated with the monomer/IL mixture viscosities determined by viscosity synergism. Moreover, the relative difference between the viscosity of the monomer and the IL (with or without viscosity synergism) may decide what affects the polymerization rate more: an increase in k_p (which may be enhanced, depending on conditions, by a factor up to 4 [5]) or a decrease of k_t^b (when viscosity of the IL exceeds monomer viscosity by more than one order of magnitude).

As was found in the present work, the k_p values are dependent mainly on the anion structure, which confirms earlier reports that the influence of ILs on k_p is associated with their polarity. Interactions between the monomer molecules and the ILs occur mainly with the participation of the carbonyl group in the monomers and C_2–H group of the imidazolium ring, as was shown by spectroscopic studies; the polymerization rate was found to be directly related to the magnitude of the monomer/IL interaction.

Referring to the photochemical initiation, the effect of ILs on primary and secondary photochemical processes occurring during initiation is yet not known although some photochemical reactions related to Type II photoinitiating systems were studied [38]. Thus, investigation in this field is needed and is now in progress.

Finally, it should be stressed that the basic kinetic relations found in this work should not be limited only to the photoinitiated polymerization, but should also be true for other radical polymerizations carried out in the presence of ILs.

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