

Photopolymerization kinetics and molecular interactions in methacrylate-imidazolium based ionic liquid systems

Ewa Andrzejewska^{1),*}, Agata Dembna¹⁾

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Abstract: Photopolymerization of poly(ethylene glycol) monomethacrylate (PEGMM) in two imidazolium based ionic liquids (ILs) differing with the anion size and H-bond accepting ability, i.e. 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF₄]) and 1-ethyl-3-methylimidazolium trifluoroacetate ([EMIm][ATF]) was investigated to find the effect of the IL anion on propagation k_p and termination rate k_t^b coefficients (by DSC) as well as molecular interactions in the system (on the basis of viscosity and FT-IR measurements). Polymerizations in bulk and in tricresyl phosphate (TCP) served as references. Both monomer/IL systems show strong viscosity synergism and viscosity deviations are positive indicating that viscosity of associates between the monomer and the ILs is relatively higher than that of pure components. The increase in k_p values observed in ILs is higher for polymerization in [EMIm][BF₄], which shows stronger Coulomb cation-anion attractions and lower H-bond accepting ability of the anion. The influence of the ionic liquids on the termination rate coefficient results from the viscosity of the monomer-IL system, taking account of viscosity synergism. On the basis of changes of imidazolium ring CH groups vibrations and carbonyl stretching vibrations (both in PEGMM and IL anion) two possible configurations of monomer-IL interactions were proposed: between the monomer carbonyl and C(2)-H hydrogen of the imidazolium cation in the case of [EMIm][BF₄] and a configuration in which the monomer carbonyl interacts with the imidazolium cation located on the top of the ring, in the case of [EMIm][ATF].

Keywords: photopolymerization, ionic liquid, kinetics, synergism of viscosity, molecular interactions.

Kinetyka fotopolimeryzacji i oddziaływania międzycząsteczkowe w układach metakrylan-imidazoliowa ciecz jonowa

Streszczenie: Zbadano kinetykę fotopolimeryzacji (metodą DSC) monometakrylanu glikolu polietylenowego (PEGMM) w dwóch cieczach jonowych (ILs) różniących się wielkością anionu oraz jego zdolnością elektronoakceptorową tworzenia wiązań wodorowych (HBA), tj. w tetrafluoroboranie 1-etylo-3-metyloimidazoliowym ([EMIm][BF₄]) i trifluoroocianie 1-etylo-3-metyloimidazoliowym ([EMIm][ATF]). Dla porównania przeprowadzono fotopolimeryzację w masie i w fosforanie trikrezylu (TCP). Obydwa układy PEGMM/IL wykazują silny synergizm lepkości — lepkość asocjatów pomiędzy monomerem i IL jest większa, niż związków wyjściowych (rys. 1). Określono wpływ IL na przebieg polimeryzacji. Wyznaczono współczynniki szybkości propagacji k_p i terminacji k_t^b w funkcji stopnia przereagowania wiązań podwójnych (rys. 3). Obserwowany wzrost k_p w IL jest większy w przypadku polimeryzacji w [EMIm][BF₄], która cechuje się silniejszym oddziaływaniem kulombowskim kation-anion oraz słabszą HBA anionu. Wpływ IL na k_t^b jest zgodny z ich wpływem na lepkość układu ($k_t^b \sim 1/\eta$) przy uwzględnieniu synergizmu lepkości. Na podstawie położenia pasm odpowiadających drganiom grup CH pierścienia imidazoliowego oraz drgań rozciągających karbonylu (zarówno w monomerze, jak i w anionie IL, rys. 4 i 5) zaproponowano dwie możliwe konfiguracje oddziaływań pomiędzy monomerem a IL: pierwszą pomiędzy karbonylem monomeru a wodorem grupy C(2)-H pierścienia imidazoliowego (w przypadku [EMIm][BF₄]) oraz drugą, w której karbonyl monomeru oddziałuje z kationem będąc usytuowany ponad płaszczyzną pierścienia.

Słowa kluczowe: fotopolimeryzacja, ciecz jonowa, kinetyka, synergizm lepkości, oddziaływania międzycząsteczkowe.

¹⁾ Poznan University of Technology, Faculty of Chemical Technology, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznan, Poland.

^{*)} Corresponding author; e-mail: ewa.andrzejewska@put.poznan.pl

In recent years ionic liquids (ILs) were widely studied as polymerization media in various types of polymerization processes, like free-radical polymerization, living/controlled radical polymerization (e.g. ATRP), reversible addition-fragmentation transfer (RAFT), or ionic and

coordination polymerizations [1]. In the case of radical processes, polymerization rate and polymer molecular weight in IL solution were enhanced as compared to polymerization in conventional organic solvents or in bulk. This resulted both from a significant increase of the propagation rate coefficient (k_p), as well as a decrease of the bimolecular termination rate coefficient (k_t^b). IL polarity was suggested to be the most probable origin of the k_p enhancement [2–4], whereas high viscosity of ILs was responsible for the decrease of k_t^b [4, 5]. To obtain more information how the IL polar environment influences k_p , the experimental data were correlated to Kamlet-Taft solvatochromic parameters, which enabled differentiation between hydrogen bond-donating (HBD), hydrogen bond-accepting (HBA), and dipolarity/polarizability effects on k_p [6–8]. It was found that the strongest contribution to the solvent induced variations in k_p have dipolarity and polarizability [9]; contribution from H-bond donating ability of the IL is of lower importance.

The interaction between a monomer and a solvent (IL) is usually evaluated by a shift of the monomer carbonyl peak in FT-IR spectra. All solvents resulting in a lowering of the carbonyl absorption wavenumber are associated with a solvent induced enhancement of k_p [9]. The lack of the appearance of the bimodal C=O absorption peak indicates that there is no classical hydrogen bonding between the weakly acidic C(2)-H hydrogen atom at the heterocyclic ring of the IL cation and the carbonyl group of the monomer. The shift of the monomer carbonyl stretching vibration is rather associated with alteration of the electron density of the C=O bond due to formation of charge separated monomer resonance structures which are favored by ILs [2]. Because C=O and C=C bonds are conjugated, the electron density of the double bond is also affected, which changes the monomer reactivity toward radical attack.

Although the frequency shift of the C=O peak in relation to polymerization kinetics was discussed in a number of papers [2, 3, 5, 9, 10], information about the corresponding shift of vibrations of functional groups in IL is rather insignificant [5]. Changes in frequencies of C-H vibrations of imidazolium cation and vibrations of the accompanying anion were mainly discussed in terms of cation-anion and IL-solvent interactions and structure [11–14].

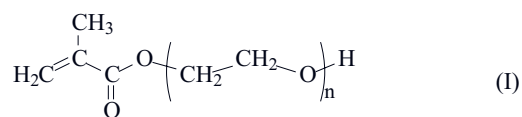
In the present work we undertook investigations of the photoinduced polymerization of a model monomer, poly(ethylene glycol) monomethacrylate (PEGMM) in two imidazolium based ILs differing with the anion size and H-bond accepting ability, i.e. 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm][BF₄]) and 1-ethyl-3-methylimidazolium trifluoroacetate ([EMIm][ATF]) {hydrogen bond accepting ability (HBA) of the [CF₃COO]⁻ is higher than that of [BF₄]⁻, which is a non-HBA anion [8]}. Polymerizations in bulk and in a non-ionic diluent of medium polarity, tricresyl phosphate (TCP), served as references. The influence of the IL

structure on propagation and termination rate coefficients as well as molecular interactions in the system (on the basis of viscosity and FT-IR measurements) were investigated and probable configurations of monomer-IL interactions were proposed.

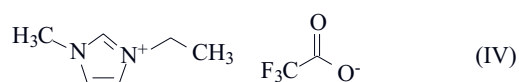
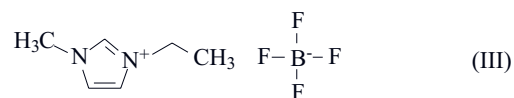
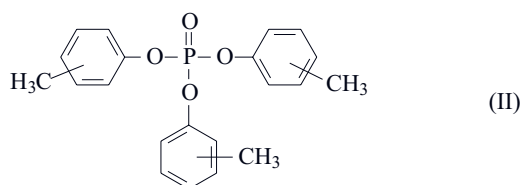
EXPERIMENTAL PART

Materials

Poly(ethylene glycol)monomethacrylate [PEGMM, formula (I), $\bar{M}_w = 360$, viscosity at 40 °C $\eta^{40} = 20.0$ mPa · s], tricresyl phosphate [TCP, formula (II), $\eta^{40} = 23.3$ mPa · s] and 2,2-dimethoxy-2-phenylacetophenone (DMPA, photoinitiator) were delivered by Sigma-Aldrich. The mono-



$n = 6.2$



mer was purified by column chromatography before use and was stored over molecular sieves. 1-Ethyl-3-methylimidazolium tetrafluoroborate {[EMIm][BF₄], formula (III), $\eta^{40} = 24.8$ mPa · s} and 1-ethyl-3-methylimidazolium trifluoroacetate {[EMIm][ATF], formula (IV), $\eta^{40} = 15.4$ mPa · s}, both of high purity (>99.0 %, water content <1 %, halide content <100 ppm), were supplied by Merck.

Methods of testing

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 O₂) using the Pyris 6 instrument (Perkin-Elmer) equipped with a lid especially designed for photochemical measurements.

The samples (2 mg) were polymerized in open aluminum pans with a diameter of 6.6 mm. The polymerizations were initiated by the light from a LED lamp (Hamamatsu LC-L1 with maximum emission at 366 nm, light intensity at the sample pan position was 1 mW/cm² for

determination of polymerization rates and 1.5 mW/cm^2 in experiments for determination of the polymerization rate coefficients) in the presence of 1 wt % of DMPA. All DSC photopolymerization experiments were conducted at least in triplicate. The reproducibility of the results was about $\pm 3 \%$. For computations, the heat of polymerization was taken to be 56 kJ/mol [5].

The experimental data for calculations of the polymerization rate coefficients were obtained from postpolymerization processes registered under non-stationary conditions (after stopping the irradiation at various degrees of double bond conversion). The detailed procedure is described in [5].

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 of 10–160 rpm. The viscosity deviation ($\Delta\eta$) was calculated from the equation [15]:

$$\Delta\eta = \eta_{mix} - \sum_{i=1}^2 x_i \eta_i \quad (1)$$

where: η_{mix} — the mixture viscosity, x_i — mole fractions, η_i — individual component viscosity.

IR spectra were recorded as thin films between KBr windows on Nexus Nicolet model 5700 FT-IR spectrometer with spectral resolution 1 cm^{-1} .

RESULTS AND DISCUSSION

Photopolymerization rates

The selected monomer (PEGMM) is a monomethacrylate, which is well soluble in the ILs used and its polymer is fully compatible with these ILs forming a homogeneous gel. Thus, polymer precipitation (often observed in ILs) will not affect the polymerization kinetics.

Kinetic curves of the polymerization in ILs are rarely presented in articles, although they provide much important kinetic information. In this section we discuss the influence of $[\text{EMIm}][\text{BF}_4]$ on various stages of polymerization by comparing kinetic curves obtained in the pre-

sence of this IL and TCP. Since the viscosity of the two solvents at the polymerization temperature was almost the same and similar to the viscosity of the monomer, a significant effect of variations in viscosity with the change in the monomer/solvent molar ratio on the polymerization should not be expected.

Polymerization rates (R_p) versus conversion (p) curves obtained at various solvent concentrations are shown in Fig. 1. The curves drawn for TCP (Fig. 1a) reflect classical solvent effect on polymerization: gradual disappearance of the gel effect with increasing monomer dilution followed by a decrease of the initial rate (in our case at the concentration higher than 30 wt % of TCP). The final double bond conversion significantly increases, indicating the plasticizing effect of TCP.

In the IL (Fig. 1b) the polymerization proceeds in a completely different manner. Gel effect is enhanced at lower IL contents and disappears at higher solvent content, but in the whole range of IL concentrations the polymerization occurs with significantly increased initial rates. Conversion increases only slightly. Whereas acceleration of the polymerization can result in part from the expected increase in k_p , the enhancement of the gel effect is often associated with an increase in initial viscosity of the system to be polymerized (due to reduction of the diffusion-controlled k_t^b). As it will be shown in the next section, despite the fact that the viscosities of the monomer and the IL are similar, viscosities of their mixtures can be much higher, which may be the cause of the observed phenomenon.

Viscosity

As mentioned earlier, the initial viscosity of a polymerizable composition is an important factor influencing k_t^b (an inverse proportionality). Generally, significant decrease in viscosity of ILs is observed on addition of a co-solvent of low viscosity [16, 17]. Organic co-solvents „solvate” the constituent ions in the IL, causing a decrease in the aggregations of these ions [16]. Thus, the

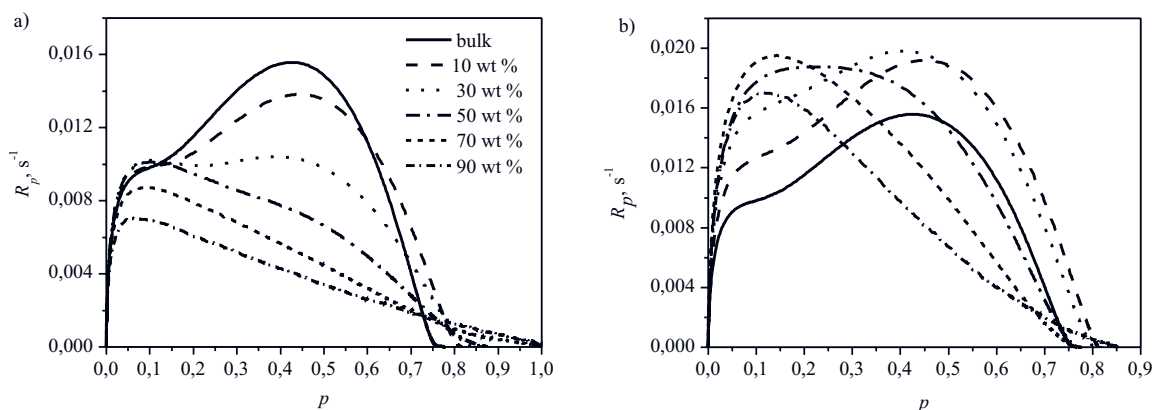


Fig. 1. Polymerization rate (R_p) versus conversion (p) curves for PEGMM polymerization (at $40 \text{ }^\circ\text{C}$) using various concentrations of solvent: a) TCP, b) $[\text{EMIm}][\text{BF}_4]$

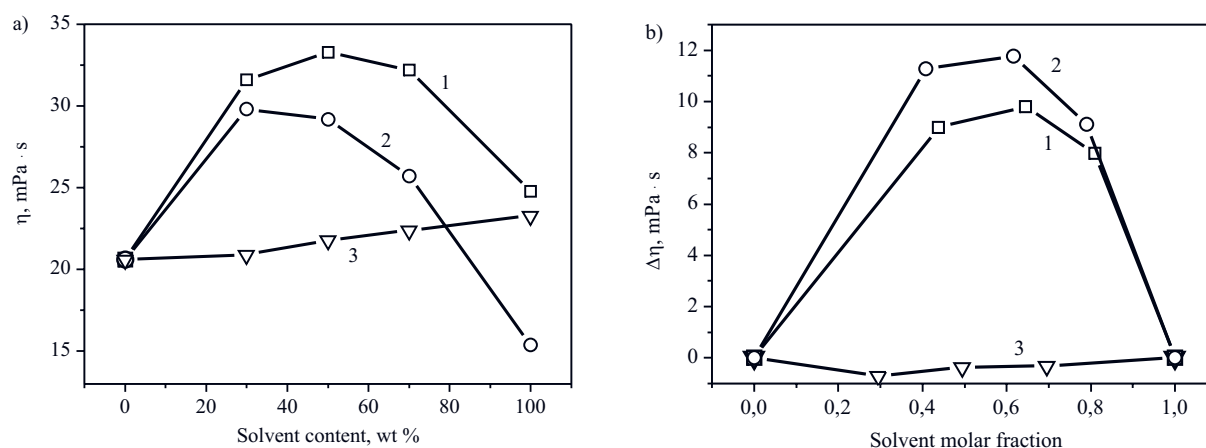


Fig. 2. Viscosity of the PEGMM/solvent blends (a) and viscosity deviation (b), both as functions of solvent concentration at 40 °C: 1 – [EMIm][BF₄], 2 – [EMIm][ATF], 3 – TCP

magnitude of changes in viscosity strongly depends on the solvent added.

Viscosity provides also information on molecular interactions between the components. For pure ILs, a higher viscosity indicates stronger cation-anion interactions (e.g. [EMIm][BF₄] versus [EMIm][ATF]). On the other hand, localized directional hydrogen bonding between C(2)-H bond of the imidazolium cation and the anion results in decreased viscosities [18], which in turn is in agreement with higher H-bond accepting ability of the [ATF]⁻ anion.

The viscosities of the monomer-solvent systems for the two ILs and TCP were measured as a function of the solvent concentration (Fig. 2a).

As can be seen, the mixtures of the monomer with both ILs show markedly higher viscosities than the individual components, which indicates a strong viscosity synergism. The maximum effect occurs for compositions containing about 50 wt % of ILs, which corresponds to about 0.60–0.65 mol fraction. This behavior is analogous to that reported by us earlier [5] and indicates strong specific interactions between the ILs and monomer molecules. Pure imidazolium based ILs form an extended hydrogen bonded network due to self-aggregation of monomeric cations under the influence of anions [11]. We can suppose that whereas addition of lower amounts of ILs to the monomer leads to formation of strong associates, at high content IL aggregates entrap monomer molecules [11]. No synergism was observed in the case of TCP.

Intermolecular interaction can be better described by viscosity deviation $\Delta\eta$ (Fig. 2b). The viscosity deviation represents deviations from a rectilinear dependence of viscosity on mole fraction [15] (qualitatively analogous results we obtained for excess logarithm viscosity). For monomer – ILs mixtures $\Delta\eta$ versus IL content passes through a maximum, while the curve as a whole is not symmetric indicating on the strongest interactions at about 6:4 IL to monomer molar ratio. The positive values of viscosity deviation of the system suggest that viscosities of associates formed between PEGMM and ILs are

relatively higher than those of pure components [16] and this deviation is larger in PEGMM/[EMIm][ATF] system (higher $\Delta\eta$ values).

It is worthy to noteworthy that positive viscosity deviations for monomer/IL systems were observed only by us, but for instance, in the case of mixtures of [BMIm][PF₆] with organic solvents (THF, DMSO, methanol) negative viscosity deviations were observed [15, 16].

Polymerization rate coefficients

The propagation and termination rate coefficients (k_p and k_t^b , respectively) were estimated for the polymerization in the presence of 70 wt % of the solvent, which was one of the two ILs or TCP (for comparison). The R_p versus p curves are presented in Fig. 3a.

Polymerization occurs much faster in [EMIm][BF₄] than in [EMIm][ATF] indicating a significant influence of IL anion on the polymerization kinetics.

The photopolymerization rate (R_p) is described by the following expression:

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

where: [M] – the double bond concentration, ϕ – quantum yield of initiation, I_a – intensity of the light absorbed.

The rate coefficients were calculated in the form of $k_p \cdot F$ and $k_t^b \cdot F$, where $F = (\phi \cdot I_a)^{0.5}$. F was assumed to be constant in the range of conversions studied. These parameters were used to find the trend followed by true k_p and k_t^b coefficients. The estimated parameters as a function of conversion are shown in Fig. 3b. The k_t^b coefficients decreases only slightly and k_p remains practically constant in the conversion range studied, which is associated with the high dilution of the monomer.

Looking at the results it is clear why the polymerization in [EMIm][BF₄] is the fastest – the k_p values in this IL are the highest, whereas the values of k_t^b are the lowest [compare eq. (2)]. In the case of [EMIm][ATF] the k_p is lower and k_t^b is higher than it was observed for reaction in

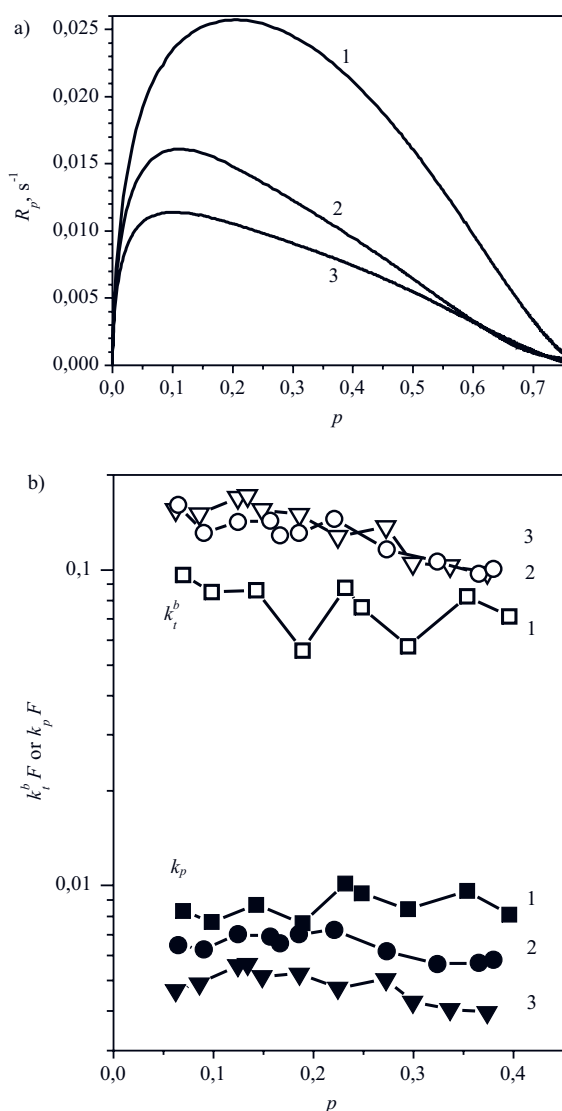


Fig. 3. PEGMM photopolymerization in the presence of 70 wt % of the solvent (1 – [EMIm][BF₄], 2 – [EMIm][ATF], 3 – TCP) at 40 °C: a) polymerization rate (R_p) versus double bond conversion curves (p), b) parameters related to propagation ($k_p F$) and termination ($k_t^b F$) rate coefficients as a function of double bond conversion

[EMIm][BF₄], which results in lower reaction rates. Thus, higher values of k_p in [EMIm][BF₄] suggest that this IL better stabilizes charge separated monomer resonance structures. As expected, k_p is the lowest for the polymerization in TCP but k_t^b is slightly higher (at low conversions) than in [EMIm][ATF], despite much lower viscosity of the latter. However, the increasing order of k_t^b in solvents [EMIm][BF₄] < [EMIm][ATF] ≤ TCP is in agreement with the dependence $k_t^b \sim \eta^{-1}$ due to synergism of viscosity (compare Fig. 2a at the 70 wt % solvent concentration).

The answer to the question whether the higher rates of reaction in ILs relative to TCP are more due to higher k_p or lower k_t^b values gives the following estimation. The polymerization rates in [EMIm][BF₄] and in [EMIm][ATF] (near the maximum values, at 10 % of conversion) are

2.05 and 1.41, respectively, times higher, than in TCP. This increase is higher than the increase in k_p , which is about 1.42 and 1.28 times, respectively. On the other hand, the k_t^b values in ILs are lower than in TCP by a factor of 1.84 (for [EMIm][BF₄]) and 1.14 (for [EMIm][ATF]), which increases the polymerization rate by a factor of 1.36 and 1.07, respectively (inverse square root dependence), i.e. to a lesser degree than the acceleration resulting from the increase in k_p (direct proportionality). This clearly shows that for our systems higher reaction rates in ILs compared to TCP are due more to higher k_p than lower k_t^b .

The polymerization rate coefficients for the neat PEGMM were determined in our previous paper [5] at very similar conditions. A very rough estimation based on comparison of the k_p and k_t^b values from our current and previous paper seems to indicate that for the systems studied the accelerating effect of ILs on the PEGMM photopolymerization results also more from the increase in k_p than from the decrease in k_t^b (in contrast to systems described in [4]).

Spectroscopic investigations

As it was mentioned above, the position of the carbonyl group absorption is usually taken as a qualitative measure of relative strengths of polar interactions in monomer/IL system [19].

The influence of increasing amounts of ILs on the monomer carbonyl stretching is presented in Fig. 4. An apparent shift to lower frequencies is observed in the presence of both ILs. It is in agreement with the observation that all solvents resulting in lowering of carbonyl vibration are associated with a solvent-induced enhancement

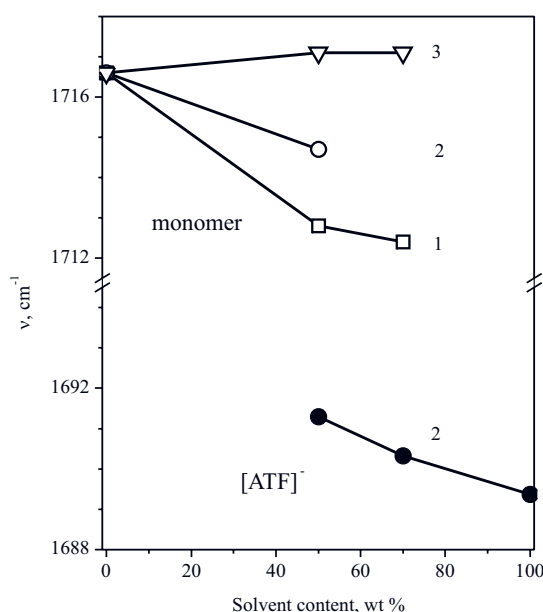


Fig. 4. Wavenumbers for stretching vibrations of the carbonyl group in the monomer and the [ATF]⁻ anion as functions of the solvent content: 1 – [EMIm][BF₄], 2 – [EMIm][ATF], 3 – TCP

of k_p [9]. Because no bimodality of the peak appeared, it proves that:

- no important H-bonding in the neat PEGMM occurs,
- the carbonyl shift is rather not associated with the classical hydrogen bonding [19].

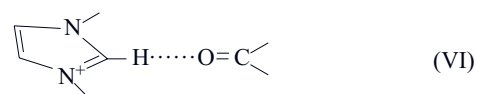
However, this shift indicates a weakening of the C=O bond, possibly due to formation of charge separated monomer resonance structures, as mentioned earlier. Larger shift observed in [EMIm][BF₄] suggests a stronger monomer – IL interaction than in the case of [EMIm][ATF] (due to overlapping of the carbonyl peaks from the monomer and from the IL, the position of the carbonyl stretching vibrations could be found only at the presence of 50 wt % of the solvent).

In the ILs spectra vibrations of the cations depend both on the conformational changes and on the association with the anion. The formation of the ion pairs influences mainly stretching and out-of-plane vibrations of the imidazolium C-H groups and stretching vibrations of the perfluoroanions. Imidazolium cation exhibits two aromatic stretching bands ca. 3140–3170 and ca. 3090–3125 cm⁻¹ ascribed to, presented in formula (V), C(4,5)-H



and C(2)-H vibrations, respectively [14]. This spectral region shows the characteristic C(2)-H...anion H-bonding modes relating to the interaction of the imidazolium cations with the anions [12–14].

Addition of increasing amount of the monomer to [EMIm][BF₄] shifts CH stretching vibrations of the imidazolium cation to lower frequencies (Fig. 5) indicating weakening of the C(4,5)-H and C(2)-H bonds. This corresponds well with analogous changes in C=O vibrations of the monomer and reflects interactions between these two compounds. Theoretical calculations suggest that in imidazolium salts weakly coordinating perfluoroanions are mainly situated near C(2)-H hydrogen but the small shift of ν C(2)-H indicates that the H-bond is weak and can be easily destroyed by a non-ionic solvent (the ions in [EMIm][BF₄] are held together mainly by strong Coulomb attractions) [14]. Thus, we may expect that H-bond type interactions between imidazolium ring and the monomer are stronger than between the cation and anion



and occur mainly between C(2)-H hydrogen and monomer carbonyl group, as shown in formula (VI). But we cannot exclude interactions with C(4,5)-H hydrogen atoms.

In the case of [EMIm][ATF] a small blue shift of the imidazolium ring CH groups vibrations is observed (Fig. 5), which means that these groups experience a slight strengthening and hence the hydrogen bonds with the anion are weakened. This is in agreement with the blue shift of the [ATF]⁻ carbonyl vibrations (Fig. 4) associated with C=O bond strengthening. These phenomena can be explained by a configuration where the carbonyl group of the monomer is on the top (or below) of the imi-

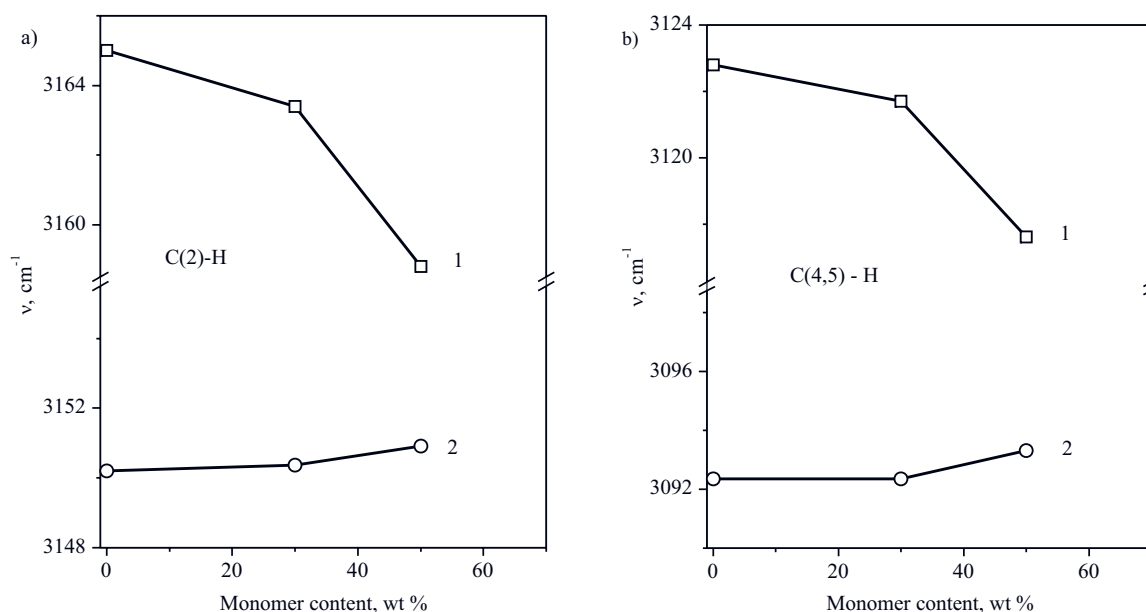
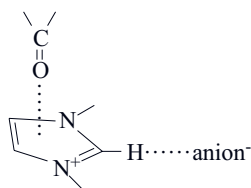


Fig. 5. Wavenumbers for an imidazolium ring CH group vibrations as a function of the monomer content: 1 – [EMIm][BF₄], 2 – [EMIm][ATF]



(VII)

dazolium ring [formula (VII)]. Charge from the monomer carbonyl is transferred to and distributed over the imidazolium ring which causes strengthening of its C-H bonds, weakening of the interionic H-bonds and subsequent shortening of the C=O bond in the IL anion. This type of interaction between [EMIm][EtSO₄] and acetone was proposed recently [12].

The difference in interaction between the two ILs and the monomer results mainly from the size and properties of the anions. The small [BF₄]⁻ anion is sterically less demanding and its hydrogen bond accepting ability is lower; this enables the monomer carbonyl group to approach the C(2)-H hydrogen and to interact with it. On the other hand, the [ATF]⁻ anion is larger and causes shielding of the C(2)-H hydrogen; moreover it forms stronger H-bond with the cation. Thus, the interaction in which the methacrylate group is located on the top of the cation is more probable.

CONCLUSIONS

Kinetics of photopolymerization in ILs and monomer-IL interactions were investigated for two ILs differing in the anion size and H-bonding ability and compared to a non-ionic solvent. The both monomer/IL systems show strong viscosity synergism which should be taken into account when the effect of IL viscosity in the polymerization rate is considered. Viscosity deviations are positive indicating that viscosity of associates between the monomer and the ILs is relatively higher than those of pure components.

The increase in k_p values is higher when the polymerization is carried out in the IL with the anion which shows stronger Coulomb attractions with the cation and lower H-bond accepting ability ([BF₄]⁻). The influence of the ionic liquids on k_i^b results from the viscosity of the monomer – IL system, taking account of viscosity synergism.

Analysis of changes of imidazolium ring CH group vibrations together with changes in carbonyl stretching vibrations (both in PEGMM and [ATF]⁻) allowed us to propose probable configurations of monomer-IL interactions. The methacrylate carbonyl can interact with C(2)-H hydrogen of the imidazolium cation or can be situated on the top of the ring, depending on the size of the IL anion and its H-bonding ability. However, it is difficult to say whether these configurations have deeper influence on the polymerization rate; the most important is polarity/polarizability, which is the higher, the smaller the ions are [20].

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