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Ionic Liquids as Advantageous Reaction Media for Free Radical Polymerization

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Summary: Ionic liquids are attractive solvents for polymer synthesis because their properties can be easily and broadly tuned by varying the structure of both the cation and the anion. Application of ionic liquids as reaction medium for free radical polymerization of vinyl monomers, such as methacrylates or styrene, results in high yields and high molecular weights of the polymers. Reasons for these effects are only partially due to the high viscosity of ionic liquids, which may reduce bimolecular termination of the propagating chains, but are also due to solvent cage effects that differ from those in traditional organic solvents because of strong ionic interactions between the individual ions of the ionic liquids. Furthermore, the high dissolving power of ionic liquids for both weakly polar as well as highly polar monomers makes ionic liquids interesting as solvents for statistical copolymerization. Interestingly, variation of the alkyl chain length of substituents at the cation of the ionic liquid allows altering of copolymer composition.

Keywords: copolymerization; degree of polymerization; ionic liquid; polymethacrylates; polystyrene; radical polymerization; structure-property relations; viscosity

Introduction

Free radical polymerization is the mostly applied mechanism to manufacture polymers because of high polymerization rate and tolerance to many functional groups bound at monomers.[1] Often, a solvent is used to avoid the Trommsdorff-Norrish effect.[2,3] Solvents do not only reduce the polymerization rate and improve heat transfer during polymerization, they also may strongly influence both the polymerization process and the polymer structure.[4,5]

Ionic liquids have received increased interest among modern solvents virtue of their negligible vapor pressure, and of the possibility to tailor their dissolution capability by variation of the structures of either one or both ions constituting the ionic liquids.[6–8] The structure of ionic liquids can be varied in a huge range covering various anions, such as small anions, e.g., tetrafluoroborate, hexafluorophosphate, and dicyanamide, or anions with apolar alkyl or aryl substituent, e.g., octyl sulfate or tosylate, or anions with delocalized charge, e.g., bis(trifluoromethylsulfonyl)imide. The structure of the ionic liquid cation can be varied analogously. This includes for example imidazolium, pyridinium and ammonium ions that are substituted with alkyl groups of different lengths at the nitrogen, or with additional substituents at the carbon atoms of the aromatic rings. Structure variation results in changes of viscosity and polarity of ionic liquids.[9–11] This opens a high application potential of ionic liquids on the one hand, but renders the selection of appropriate ion pairs intricate for a given application, if the structure property relations are not well known.

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Ionic liquids have been investigated in radical polymerization since several years[12–55] as summarized and discussed in several reviews.[56–59] Compared to the use of traditional solvents, rates of polymerization are mostly higher in ionic liquids, and molecular weights are often increased.[29,33,34] In certain cases, the achieved molecular weights are even higher when polymerized in ionic liquids than when prepared in bulk.[34,45] Furthermore, molecular weights and molecular weight distributions were found to be sensibly affected by variation of the cation or the anion of the ionic liquid employed.[34] For instance, the increase of the length of alkyl substituents at the nitrogen of imidazolium cations typically increases viscosity and decreases polarity and micropolarity, respectively.[9,10] Furthermore, an additional methyl substituent at the 2-position of the imidazolium ring increases viscosity as well. Nonetheless, hydrogen bonding between the acidic hydrogen atom at the 2-position at the imidazolium ring and any hydrogen acceptor is thus reduced in comparison to simple 1-alkyl-3-methylimidazolium based ionic liquids.[60] The variation of the behavior of ionic liquids is more difficult to predict when the nature of the anion is varied, as cation-anion interactions affect the properties much more than a simple change of the substituent size at the cation.[60,61] Electrostatic interactions, hydrogen bonding, and van der Waals interactions in ionic liquids contribute to the solubilization behavior of monomers, which is important for copolymerization of monomers of strongly differing polarity, e. g. of hydrophilic and hydrophobic monomers.[29,33,41] Moreover, solvent cage effects may be important regarding the efficient formation of initiating radicals in free radical polymerization. Investigation of photogenerated model radicals and their recombination in the dark as function of both ionic liquid structure and temperature gives information about the influence of radical diffusion and solvent cage on radical recombination in ionic liquids.[62,63] The understanding of these effects may help to select the most suitable ionic liquids for radical polymerization processes.

In this context, the results presented shall contribute to a better understanding of the role of ionic liquids in free radical polymerization. Methacrylates of both low and high polarity, as well as styrene were selected as model monomers for polymerization in ionic liquids. The ionic liquids employed comprise imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate, triflate, octylsulfate, dicyanamide, tosylate and bis(trifluoromethyl)sulfonylimide anions as well as pyrrolidinium and tetraalkylammonium bis(trifluoromethylsulfonyl)imides. Additionally, one alkyl substituent of the imidazolium, pyrrolidinium or tetraalkylammonium cations was varied. These structural variations modulate both viscosity and polarity of the ionic liquids. This paper focuses on the influence of the ionic liquid structure on molecular weight and polydispersity of the model homopolymers, and on the influence on the composition of the statistical methacrylate copolymers combining both hydrophilic and hydrophobic comonomers, i.e., of copolymers of marked amphiphilic character.

Polymethacrylate Synthesis in Ionic Liquids

Ionic liquids bearing bis(trifluoromethylsulfonyl)imide or dicyanamide as anion (Figure 1) belong to room temperature ionic liquids exhibiting rather low viscosity.[63,64] Therefore, such ionic liquids seemed particularly suitable for free radical polymerization of methacrylates, and thus were primarily engaged. Indeed, such ionic liquids proved to be useful reaction media, and give rise to high molar mass polymers, as exemplified in Figure 2 for polybenzylmethacrylate. As common feature, samples made in the ionic liquids **1–4** show rather broad molecular weight distributions. Apart from that, significant differences in the molecular weight distributions of polybenzylmethacrylate are observed between

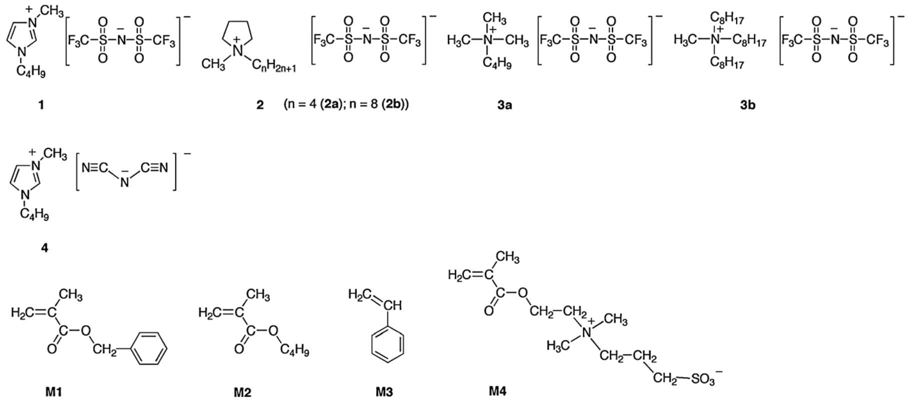

Figure 1.
Chemical structure of ionic liquids and of the monomers used in the free radical polymerization studies: (1-butyl-3-methylimidazolium (**1**), 1-alkyl-1-methylpyrrolidinium (**2a** (n = 4); **2b** (n = 8)), tetraalkylammonium based ionic liquids **3a** and **3b** bearing bis(trifluoromethylsulfonyl)imide as anion, and 1-butyl-3-methylimidazolium dicyanamide (**4**); monomers: (benzylmethacrylate (**M1**), *n*-butylmethacrylate (**M2**), styrene (**M3**), and zwitterionic methacrylate bearing a sulfobetaine moiety (**M4**)).

polymerizations conducted in the imidazolium (**1**, **4**) or pyrrolidinium (**2a**, **2b**) based ionic liquids, and those based on tetraalkylammonium cations (**3a**, **3b**) although comparable reactions conditions (1 mole-% azobis(isobutyronitrile) (AIBN); 70 °C; 24 h polymerization time) were used for all polymerization experiments. The tetraalkylammonium bis(trifluoromethylsulfonyl)-imides **3a** and **3b** result in pronounced bimodal distributions with more or less separated higher molecular weight fractions, which are absent in the case of imidazolium (**1** and **4**) and pyrrolidinium (**2**) based ionic liquids. According to the values listed in Table 1, viscosity cannot explain the occurence of higher molecular weight fractions when using the aliphatic ammonium based ionic liquids. In fact, the viscosity of **3a** is relatively low while the viscosity of **3b** is at the upper end of the viscosity range covered by the various ionic liquids investigated. Nevertheless, the average degree of polymerization obtained by free radical polymerization in ionic liquids tends to correlate more or less with their viscosity (Figure 3).[36] We note also that polymer yields differ substantially under otherwise identical conditions when using ionic liquids **1**–**4**, as summarized in Table 1. Yields were particularly high if butyl substituted imidazolium or pyrrolidinium bis(trifluoromethylsulfonyl)imides (**1** and **2a**) were used for polymerization, while the use of the other ionic liquids gave considerably lower yields although reaction conditions were identical. Despite the differing yields, weight average molecular weights (M_w) are surprisingly similar when using **1**, **2**, and **4** as reaction media (Table 1).

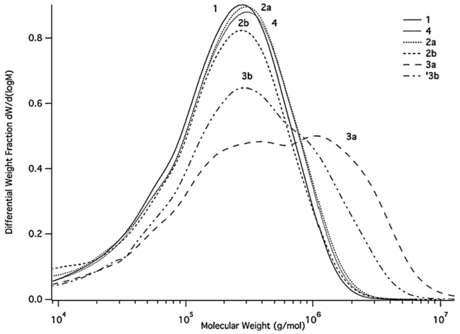

Figure 2.
GPC elugrams of polymer samples obtained by free radical polymerization of **M1** in selected ionic liquids (**1**; **2a**; **2b**; **3a**; **3b**; **4**) using AIBN (1 mole-% relative to the monomer) as initiatior at 70 °C for 24 h.

Although differences in viscosity alone cannot explain the differences in the molecular weight of the polymers obtained,

Table 1.
Yield number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (PDI) of polybenzylmethacrylate synthesized in the ionic liquids depicted in Figure 1 (1 mole-% AIBN relative to the monomer; 70 °C; 24 h polymerization time) including viscosity of the ionic liquids at a shear rate of $10\,s^{-1}$ at 70 °C

Ionic liquid	η_{10} (mPa·s) at 70 °C	yield (%)	Mn (g/mol)	Mw (g/mol)	PDI
1	13	92	73000	311000	4.3
2a	18	89	106000	351000	3.3
2b	26	57	87000	290000	3.3
3a	18	34	127000	1024000	8.1
3b	61	39	122000	596000	4.9
4	13	43	87000	344000	3.9

a general trend exists between ionic liquid viscosity and the degree of polymerization (X_n) made by free radical polymerization in ionic liquids (Figure 3). In any case, X_n is higher when ionic liquids are used as media for polymerization in comparison with using organic solvents, such as toluene or dimethylsulfoxide (Figure 3). As expected from theory, X_n is significantly lower in the case that organic solvents were used in radical polymerization than for polymerizations conducted in bulk. Still, polymerization in certain ionic liquids, in particular in such with increasing viscosity causes a general increase in the degree of polymerization of the polymethacrylates. The two notable exceptions of ionic liquids from this general trend exist that have viscosities higher than 50 mPa.s and longer alkyl substituents either at the cation (*N,N,N,N*-trioctylmethylammonium bis(trifluoromethylsulfonyl)imide) or at the anion (1-butyl-3-methylimidazolium octylsulfate). All other ionic liquids investigated within this row show a rough increase of the degree of polymerization of the polymer synthesized in the ionic liquids with increasing ionic liquid viscosity. Increasing viscosity of ionic liquids seems to reduce the bimolecular termination reaction of growing polymer chains, thus increasing the degree of polymerization.[65] Additionally, the propagation seems to be accelerated in many ionic liquids.[42,47]. Yet, ionic liquids with extremely high viscosity may considerably reduce diffusion of the monomer as well. This may limit the degree of polymerization. Interestingly, similar results were obtained for polybutylmethacrylate and polybenzylmethacrylate made in ionic liquids regarding molecular weight and molecular weight distribution. This suggests that the interaction of the methacrylate moiety with various ionic components of the ionic liquids plays an important role.

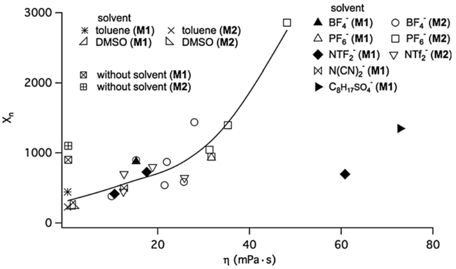

Figure 3.
Degree of polymerization of polybutylmethacrylate and polybenzylmethacrylate obtained by free radical polymerization of **M1** or **M2** in ionic liquids (imidazolium based ionic liquids bearing a variation of the alkyl group bound at the nitrogen atom of the cation and tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), octylsulfate ($C_8H_{17}SO_4^-$), bis(trifluoromethylsulfonyl)imide (NTf_2^-) or dicyanamide ($N(CN)_2^-$) as anion; pyrrolidinium and ammonium bis(trifluoromethylsulfonyl)imides (NTf_2^-)) and organic solvents (toluene, dimethylsulfoxide (DMSO)) as function of the reaction medium viscosity. Furthermore, results obtained by bulk polymerization are included as well.

Polystyrene Synthesis in Ionic Liquids

Hypothesizing that methacrylate moieties can interact with the ionic liquid via hydrogen bonding, we explored the polymerization of styrene in selected ionic liquids as hydrogen bonding is inherently absent in the case of styrene. Results are exemplified in Figure 4. We found that polystyrene samples synthesized in 1-alkyl-3-methylimidazolium tosylates show a high molecular weight fraction, which exceeds the molecular weight obtained in bulk polymerization (Figure 4). This result supports the hypothesis of protected radicals discussed in literature.[44] This hypothesis may be applied either on all radicals occuring during polymerization or just on the primary radicals that initiate the polymerization. Investigation on model radicals resulted in discussion of an increase in radical recombination within the solvent cage in ionic liquids to significantly higher extent compared to traditional organic solvents.[62,63,66] This effect may reduce the concentration of active radicals that can start polymer growth, thus increasing the molecular weight. These results may support the hypothesis that increasing radical recombination within the solvent cage results in reduced concentration of active radicals that are able to start polymer growth. Extended recombination reaction of primary radicals within the solvent cage results in reduction of primary radical concentration, and therefore, in an increase in the molecular weight of the polymer obtained. Interestingly, the content on the higher molecular weight fraction becomes smaller when the alkyl substituent at the imidazolium ion is slightly longer. The longer alkyl substituent reduces micropolarity of the ionic liquids, and enhances the compatibility of the solvent with the non-polar monomer styrene (**M3**). Therefore, the lower compatibility of **M3** with imidazolium tosylates bearing only small alkyl substituents is a further reason for the broad molecular weight distribution. The higher the compatibility of **M3** is with the imidazolium tosylate bearing one longer alkyl substituent at the cation that smaller is the molecular weight distribution.

Noteworthy, the use of a mixture of 1-ethyl-3-methylimidazolium tosylate and 1-dodecyl-3-methylimidazolium tosylate (ratio wt:wt = 1:2) as polymerization medium narrows the extremely broad molecular weight distribution, although the molecular weight of the polystyrene sample remains higher than when made by bulk polymerization (Figure 5). Obviously, the less polar ionic liquid 1-dodecyl-3-methylimidazolium tosylate is a more suitable solvent for styrene than the ethyl substituted imidazolium tosylate. Yet, as dodecyl substituted

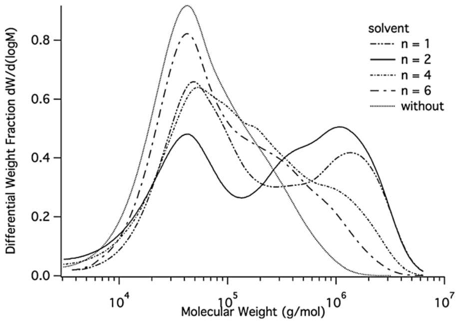

Figure 4.
GPC elugrams of polystyrene obtained by free radical polymerization of styrene (**M3**) using AIBN (1 mole-% relative to the monomer) as initiator at 70 °C in various reaction media for 24 h: 1-alkyl-3-methylimidazolium tosylates: n = 1 (methyl); n = 2 (ethyl); n = 4 (butyl); n = 6 (hexyl), and in bulk.

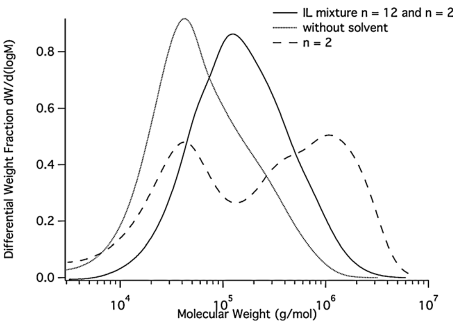

Figure 5.
GPC elugrams of polystyrene obtained by free radical polymerization of styrene (**M3**) at 70 °C using AIBN (1 mole-% relative to the monomer) in various reaction media for 24 h: 1-ethyl-3-methylimidazolium tosylate (n = 2), mixture of 1-ethyl-3-methylimidazolium tosylate (n = 2) and 1-dodecyl-3-methylimidazolium tosylate (n = 12) using weight ratio of wt: wt = 1: 2, and in bulk.

imidazolium tosylate is not useful alone for polymerization at 70 °C because its melting point is higher compared to the polymerization temperature, and crystallization occurs at the polymerization temperature even in the presence of monomer, free radical polymerization of **M3** is best conducted in the mixture of the two imidazolium tosylates. Clearly, further studies are needed to clarify this aspect.

Polarity effects of ionic liquids as discussed for polymerization of **M3** using imidazolium tosylates as matrices do not only influence the homopolymerization of this non-polar monomer they also strongly affect copolymerization of different polar monomers bearing similar polymerizable functional groups.

Copolymer Synthesis in Ionic Liquids

High solubilization power of ionic liquids for both less polar and highly polar monomers makes these solvents interesting for copolymerization of markedly differing polar monomers. This is instructively illustrated by the free radical copolymerization of the hydrophobic **M2** and the zwitterionic monomer **M4**. Both methacrylate monomers are immiscible with each other. In fact, it is even difficult to find common solvents that dissolve both monomers. The use of acetonitrile as reaction medium results in polymers that contain mainly the zwitterionic moiety **M4**.[29,33,36,41] Noteworthy, the composition of the polymers obtained is independent on the feed ratio of the monomers **M2** and **M4** if the copolymerization is conducted in acetonitrile. In contrast to this, many ionic liquids do well dissolve both monomers, and copolymers are obtained that contain both monomer units. Interestingly, the precise ionic liquid structure, especially the length of alkyl substituents at the imidazolium ion, can influence copolymer composition beyond the comonomer ratio. For example, the mole fraction of **M2** in the copolymer increases from about 0.46 when using 1-butyl-3-methylimidazolium tetrafluoroborate as solvent for copolymerization to 0.7 when the analogous ionic liquid bearing a decyl substituent served as reaction medium, though the monomer feeds contained stoichiometric amounts of **M2**: **M4** in both experiments. This clearly demonstrates that the polarity of ionic liquids is a crucial parameter for their use as reaction medium, and may be advantageously exploited to tune, e.g., the composition of copolymers of a given comonomer pair.

Conclusion

The results presented demonstrate that a number of factors such as viscosity, polarity, and solvent cage effects strongly influence the structure of polymers made in ionic liquids. Accordingly, the broad variability of the structure of ionic liquids opens huge possibilities in the field of polymer synthesis. However, the rational and successful application of ionic liquids as reaction media for synthesizing new homopolymers and copolymers requires thorough knowledge of structure-property relations of ionic liquids and of their interaction with the monomers. While certain relationships have been elucidated now, it is evident that the current state of knowledge is yet far from complete.

[1] K. Matyjaszewski, T. P. Davis, *Handbook of Radical Polymerization*, J. Wiley & sons, Inc., Hoboken **2002**.
[2] R. G. W. Norrish, R. R. Smith, *Nature* **1942**, *150*, 336.
[3] E. Trommsdorff, H. Köhle, P. Lagally, *Makromol. Chem.* **1948**, *1*, 169.
[4] J. M. G. Cowie, I. J. McEwen, D. J. Yule, *Eur. Polym. J.* **2000**, *36*, 1795.
[5] M. L. Coote, T. P. Davis, *Prog. Polym. Sci.* **1999**, *24*, 1217.
[6] V. N. Emel'yanenko, S. P. Vervkin, A. Heintz, C. Schick, *J. Phys. Chem. B* **2008**, *112*, 8095.
[7] J. M. S. S. Esperanca, J. N. C. Lopes, M. Tariq, L. M. N. F. Santos, J. W. Magee, L. P. N. Rebelo, *J. Chem. Eng. Data* **2009**, *55*, 3.
[8] D. H. Zaitsau, A. V. Yemalayeu, V. N. Emel'yanenko, A. Heintz, S. P. Verevkin, C. Schick, S. Berdzinski, V. Strehmel, *J. Mol. Liq.*, in press.

[9] V. Strehmel, H. Rexhausen, P. Strauch, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1933.
[10] V. Strehmel, R. Lungwitz, H. Rexhausen, S. Spange, *New. J. Chem.* **2010**, *34*, 2125.
[11] G. Yu, D. Zhao, L. Wu, S. Yang, X. Chen, *AIChE* **2012**, *58*, 2885.
[12] T. Sabu, K. Matyjaszewski, *Macromol. Chem. Phys.* **2001**, *202*, 3379.
[13] T. Biedron, P. Kubisa, *Macromol. Rap. Commun.* **2001**, *22*, 1237.
[14] H. Zhang, K. Hong, J. W. Mays, *Macromolecules* **2002**, *35*, 5738.
[15] S. Harrison, S. R. Mackenzie, D. M. Haddleton, *Chem. Commun.* **2002**, 2850.
[16] H. Zhang, L. Bu, M. Li, K. Hong, A. E. Visser, R. D. Rogers, J. W. Mays, *ACS Symp. Ser. 818*. In: R. D., Rogers, K. R. Seddon, Eds., American Chemical Society, Washington, DC **2002**, 114.
[17] M. G. Benton, C. S. Brazel, *ACS Symp. Ser. 818*. In: R. D., Rogers, K. R. Seddon, Eds., American Chemical Society, Washington, DC **2002**, 125.
[18] K. Hong, H. Zhang, J. W. Mays, A. E. Visser, C. S. Brazel, J. D. Holbrey, W. M. Reichert, R. D. Rogers, *Chem. Commun.* **2002**, 1368.
[19] H. Zhang, K. Hong, J. W. Mays, *Macromolecules* **2002**, *35*, 5738.
[20] S. Perrier, T. P. Davis, A. J. Carmichael, D. M. Haddleton, *Chem. Commun.* **2002**, 2226.
[21] T. Biedron, P. Kubisa, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 2799.
[22] S. Harrisson, S. R. Mackenzie, D. M. Haddleton, *Macromolecules* **2003**, *36*, 5072.
[23] T. Biedron, P. Kubisa, *Polym. Int.* **2003**, *52*, 1584.
[24] H. Ma, X. Wan, X. Chen, Q.-F. Zhou, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 143.
[25] H. Ma, X. Wan, X. Chen, Q.-F. Zhou, *Polymer* **2003**, *36*, 5072.
[26] S. Perrier, T. P. Davis, A. J. Carmichael, D. M. Haddleton, *Eur. Poly. J.* **2003**, *39*, 417.
[27] L. Cheng, Y. Zhang, T. Zhao, H. Wang, *Macromol. Symp.* **2004**, *216*, 9.
[28] M. G. Benton, C. S. Brazel, *Polym. Int.* **2004**, *53*, 1113.
[29] V. Strehmel, A. Laschewsky, H. Kraudelt, H. Wetzel, E. Görnitz, in "*Ionic Liquids in Polymer Systems*" *ACS Symp. Ser*, **2005**, 913, 17.
[30] S. Ding, M. Radosz, Y. Shen, *Macromolecules* **2005**, *38*, 5921.
[31] D. Li, Y. Zhang, H. Wang, J. Tang, B. Wang, *J. Appl. Polym. Sci.* **2006**, *102*, 2199.
[32] D. Li, Y. Zhang, H. Wang, J. Tang, B. Wang, *J. Appl. Polym. Sci.* **2006**, *102*, 4254.
[33] V. Strehmel, A. Laschewsky, H. Wetzel, *e-polymers* **2006**, 011.
[34] V. Strehmel, A. Laschewsky, H. Wetzel, E. Görnitz, *Macromolecules* **2006**, *39*, 923.
[35] J. Li, J. Zhang, Z. Liu, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4420.
[36] V. Strehmel, *Macromol. Symp.* **2007**, *254*, 25.
[37] J. Ueda, H. Yamaguchi, T. Yamauchi, N. Tsubokawa, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 1143.
[38] G. Schmidt-Naake, I. Woecht, A. Schmalfuss, *Macromol. Symp.* **2007**, *259*, 226.
[39] Y. S. Vygodskii, O. A. Mel'nik, E. I. Lozinskaya, A. S. Shaplov, I. A. Malyshkina, N. D. Gavrilova, K. A. Lyssenko, M. Y. Antipin, D. G. Golovanov, A. A. Korlyukov, N. Ignat'ev, U. Welz-Biermann, *Polym. Adv. Technol.* **2007**, *18*, 50.
[40] I. Woecht, G. Schmidt-Naake, *e-Polymers* **2007**, no. 100.
[41] V. Strehmel, H. Wetzel, A. Laschewsky, E. Moldenhauer, T. Klein, *Polym. Adv. Technol.* **2008**, *19*, 1383.
[42] I. Woecht, G. Schmidt-Naake, S. Beuermann, M. Buback, N. Garcia, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 1460, (Propagation kinetics).
[43] H. Minami, K. Yoshida, M. Okubo, *Macromol. Rapid Commun.* **2008**, *29*, 567.
[44] K. J. Thurecht, P. N. Gooden, S. Goel, C. Tuck, P. Licence, D. J. Irvine, *Macromolecules* **2008**, *41*, 2814.
[45] V. Strehmel, E. Reynaud, H. Wetzel, E. Görnitz, A. Laschewsky, *Macromol. Symp.* **2009**, *275–276*, 242.
[46] I. Woecht, G. Schmidt-Naake, *Macromol. Symp.* **2009**, *275–276*, 219.
[47] A. Jelicic, N. Garcia, H.-G. Löhmannsröben, S. Beuermann, *Macromolecules* **2009**, *42*, 8801.
[48] Z. Chen, F. Yan, L. Qiu, J. Lu, Y. Zhou, J. Chen, Y. Tang, J. Texter, *Langmuir* **2010**, *26*, 3803.
[49] V. H. Nguyen, Y. Haldorai, Q. L. Pham, S. K. Noh, W. S. Lyoo, J.-J. Shim, *Eur. Polym. J.* **2010**, *46*, 2190.
[50] P. D. Haller, R. J. Frank-Finney, M. Gupta, *Macromolecules* **2011**, *44*, 2653.
[51] D. S. Sundar, R. Vijayaraghavan, J. Subramaniam, M. Surianarayanan, A. B. Mandal, *J. Appl. Polym. Sci.* **2011**, *120*, 3733.
[52] Y. S. Vygodskii, D. A. Sapozhnikov, A. S. Shaplov, E. I. Lozinskaya, N. V. Ignat'Ev, M. Schulte, P. S. Vlasov, I. A. Malyshkina, *Polym. J. (Tokyo, Jpn.)* **2011**, *43*, 126.
[53] S. Brusseau, O. Boyron, C. Schikaneder, C. C. Santini, B. Charleux, *Macromolecules* **2011**, *44*, 215.
[54] Y. Terayama, M. Kikuchi, M. Kobayashi, A. Takahara, *Macromolecules* **2011**, *44*, 104.
[55] K. Matsumoto, B. Talukdar, T. Endo, *Polym. Bull.* **2011**, *66*, 199.
[56] P. Kubisa, *Prog. Polym. Sci.* **2004**, *29*, 3.
[57] T. Biedron, P. Kubisa, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 3454.
[58] P. Kubisa, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 4675.
[59] V. Strehmel, *Chem. Ing. Tech.* **2011**, *83*, 1443.
[60] A. Wulf, F. Fumino, R. Ludwig, *Angew. Chem. Int. Ed.* **2010**, *49*, 449.

[61] F. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* **2008**, *47*, 3830.
[62] V. Strehmel, J. F. Wishart, D. E. Polyansky, B. Strehmel, *ChemPhysChem* **2009**, *10*, 3112.
[63] S. Berdzinski, J. Horst, P. Straßburg, V. Strehmel, *ChemPhysChem* **2013**, *14*, 1899.
[64] K. Ueno, H. Tokuda, M. Watanabe, *PhysChemChemPhys* **2010**, *12*, 1649.
[65] G. Schmidt-Naake, A. Schmalfuß, I. Woecht, T. Glück, *Chem. Ing. Tech.* **2009**, *81*, 459.
[66] V. Strehmel, *ChemPhysChem* **2012**, *13*, 1649.