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Light Scattering in Diluted Solutions of Cellulose and Hydroxypropylcellulose in 1-Ethyl-3-methylimidazolium Acetate

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Abstract—Diluted solutions of cellulose and hydroxypropylcellulose in 1-ethyl-3-methylimidazolium acetate were studied by the method of static light scattering. Mean molecular masses and the size of the particles of the studied polymers in solution, as well as the values of the second virial coefficient are reported.

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Cellulose is the most widely practically used among all natural polymers: It is processed in large volumes through dissolution. A persistent search takes place for new solvents for cellulose matching the technological and environmental requirements. There are three types of processes to transfer cellulose to the dissolved state. The first one implies the use of reactive solvents, in which the formation of derivatives of cellulose occurs, or the soluble derivatives are formed directly by the substitution reactions in the heterogeneous medium. Reactive solvents (concentrated mineral acids, formic and trifluoroacetic acids, systems dimethylformamide–N_2O_4, dimethylformamide–SO_3, dimethylsulfoxide–paraformaldehyde, aqueous solutions of sodium hydroxide, etc.) form the cellulose derivatives, which then are dissolved [1–3], or the dissolution proceeds with substantial destruction up to the formation of oligomers [4]. The rayon process is also based on dissolution of a derivative of cellulose: its xanthogenate [5]. The second process of dissolution of cellulose is realized by the use of solutions of metal complexes: iron sodium tartrate, cuprammonium hydroxide $[Cu(NH_3)_4](OH)_2$, complexes $Ni–N[CH_2CH_2·NH_3]_3$ and $Cd–N[CH_2CH_2NH_3]_3$. Dissolution of cellulose in these systems is not followed by formation of stable derivatives [6–10]; the formed coordination complexes between the metal and the OH groups of the polymer readily decompose with precipitation of cellulose hydrate by the addition of the solution into the precipitating water bath.

The dissolution of cellulose through the formation of stable or unstable derivatives is used in practice for more than 100 years. However, ecological hazard of these methods of treatment connected with environmental pollution by the products of chemical reactions led to a sharp decrease in the volumes of production and, starting from 1980s, to intensive search for true (direct) solvents. Upon solvation of the cellulose hydroxy groups by the molecules of a direct solvent, as in the case of their chemical transformations, it becomes impossible to retain the original net of intermolecular hydrogen bonds, and the solvated macromolecules of the polymer are transferred into the solution. The advantage of direct dissolution is the possibility to create a closed recycling technology with multiple reuse of the same solvent in the industrial process. The number of direct solvents for cellulose, in which the process of dissolution takes place by the mechanism of solvation of the polymer macromolecules without formation of derivatives or metal complexes, is small. It includes tertiary amines *N*-oxides, hydrazine, dimethylsulfoxide with methylamine or tetrabutylammonium fluoride [11–14]. So far, the most widely practically applied for direct dissolution of cellulose is *N*-methylmorpholine

N-oxide monohydrate; in some European countries and in the US a technological process is elaborated on its basis. However, the fibers prepared by this process have shortcomings in comparison with rayon fibers: low values of elongation at break and an increased degree of fibrillization. In 2001, for dissolution of cellulose, ionic solvents were suggested consisting of the salts with bulky organic cations [15]. It was proved by the NMR method [16] that these compounds do not form derivatives of cellulose, namely, they are direct solvents. Appearance of a new class of solvents for cellulose launched intensive studies of the possibility to create a technological process for treatment of cellulose on their basis.

One of important parameters characterizing the state of a polymer in the solution and necessary for governing the properties of the obtained fibers or films is the size of the particles, which may substantially depend on the solvent. For cellulose, it is known that in the solutions of cotton linter and bacterial cellulose with the largest degrees of polymerization in the metal complex solvents the polymer is dispersed into separate macromolecules in the form of their complexes with the metal [17, 18]: the radius R_g of the polymer particles corresponds to the size of a single molecule and is equal to ~57 nm [17]. In solutions of the cellulose derivatives, the size of the particles depends on the degree of substitution. While for full substitution of all hydroxy groups the solubility at the molecular level is observed, the partly substituted cellulose derivatives do not dissolve to separate macromolecules in any of the known solvents [19, 20]. The aggregates with radius R_g up to 600 nm are, most probably, not the associates of single macromolecules but rather the residues of the original structure of the polymer [17, 21] stabilized by a large number of strong hydrogen bonds between the adjacent hydroxy groups. As a result of incomplete substitution, a part of these bonds remains uncleaved by the solvent so that the aggregates of different size are observed in solutions. By the investigation of diluted solutions of celluloses from different origins and degree of polymerization in *N*-methylmorpholine *N*-oxide by the methods of combined static and dynamic light scattering the values of parameter R_g were determined equal to 136–200 nm [17, 22], which also exceeds the size of isolated macromolecules. The size of the cellulose particles in direct solvents depends on the molecular mass [17, 22,], preliminary activation [22], and the presence of diluter [23, 24].

Therefore, the analysis of the literature data, which allow estimating the state of cellulose in solutions, shows that aggregates are present in diluted solutions of cellulose and its derivatives in most of the known solvents. A molecular degree of dispersion of cellulose can be achieved by using metal complex solvents with high complex formation constant, or by dissolving low-molecular fractions of the polymer. Poorly studied is the question on the state of cellulose and its derivatives in solutions in ionic liquids. Determination of the principal characteristics of the solutions in ionic liquids, such as mean molecular mass MM_w, radius R_g, the second virial coefficient A_2, is actual not only for elaboration of theoretical background of the technology of treatment but also for elucidation of the mechanism of interaction of the polymer with ionic liquids. Therefore, the aim of the present work was to study diluted solutions of cellulose and its derivatives in ionic liquids by the method of static light scattering.

The refractive indices of the solvents n_0 and the increments of refractive indices of solutions dn/dc required for processing experimental data and determined by light scattering are given in Table 1.

It should be noted that the obtained by us value of the increment of refractive index for the cellulose solution in 1-ethyl-3-methylimidazolium acetate of 0.06 $cm^3 g^{-1}$ is similar to that for the cellulose solutions in *N*-methylmorpholine *N*-oxide equal to 0.061± 0.007 $cm^3 g^{-1}$ [25].

Table 1. Refractive indices n_0 and the increments of refractive indices of solutions dn/dc at 25ºC

Polymer	Solvent	n_0	dn/dc, $cm^3 g^{-1}$
Cellulose	1-Ethyl-3-methylimidazolium acetate	1.5022	0.06
Hydroxypropylcellulose	1-Ethyl-3-methylimidazolium acetate	1.5022	0.06
Hydroxypropylcellulose	Ethanol	1.3591	0.15
Hydroxypropylcellulose extrtacted from 1-ethyl-3-methylimidazolium acetate	Ethanol	1.3591	0.17

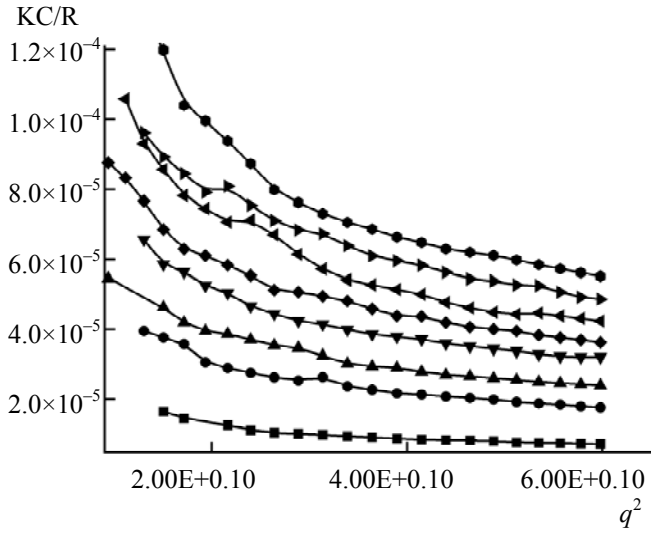

Fig. 1. Berry plot of the data of the static light scattering for hydroxypropylcellulose in ethanol.

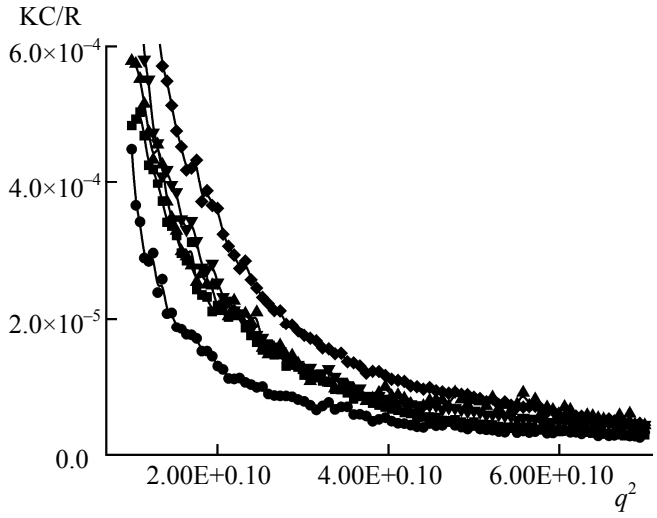

Fig. 2. Guinier plot of the data of the static light scattering for hydroxypropylcellulose in 1-ethyl-3-methylimidazolium acetate.

The data on light scattering at 25ºC plotted according to Guinier and Berry for solutions of hydroxypropylcellulose in 1-ethyl-3-methylimidazo-lium acetate and ethanol are shown in Figs. 1 and 2, respectively. The data on light scattering for solutions of hydroxypropylcellulose extracted from the ionic liquid and redissolved in ethanol are given in Fig. 3. The radius R_g and molecular mass of the hydroxy-propylcellulose particles in the studied solutions as well as the values of the second virial coefficient A_2 are given in Table 2.

The obtained values of parameters of the particles in solutions suggest that hydroxypropylcellulose in ethanol is mainly dispersed to separate macro-molecules (mean molecular mass of the particles is 1.60×10^5, radius 74 nm). Molecular mass of the hydroxypropylcellulose particles in ionic liquid is approximately 70 times higher than that of a single macromolecule, the radius of the particles reaches 188 nm; these parameters of aggregations are similar to the characteristics of the cellulose derivatives in other known solvents [17, 22]. Probably, the aggregates are the residues of the intact supramolecular structure of the polymer. The value of the radius of the particles R_g 97 nm and the molecular mass 1.51×10^6 for solutions of hydroxypropylcellulose extracted from 1-ethyl-3-methylimidazolium acetate and redissolved in ethanol allow to assume that the molecules of the ionic liquid are incorporated into the composition of these aggregates, and they cannot be removed even after 7 days of dialysis. The presence of strongly retained molecules of ionic liquid is proved by the method of thermogravimetric analysis. The TGA curves of the starting hydroxypropylcellulose and the one extracted from 1-ethyl-3-methylimidazolium acetate are shown in Fig. 4. The thermogram of the extracted sample shows two transitions: at 250 and 370ºC. The temperature of 250ºC corresponds to the start of the thermodecomposition of the ionic liquid as we have determined for pure 1-ethyl-3-methylimidazolium acetate. The second transition is connected with the thermodecomposition of the polymer. It is presumable that the molecules of the ionic liquid are strongly retained in the structure of the hydroxy-

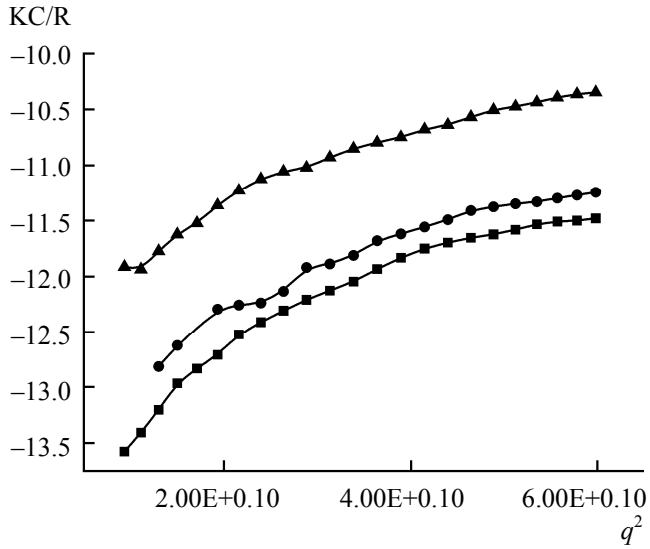

Fig. 3. Guinier plot of the data of the static light scattering for hydroxypropylcellulose extracted from 1-ethyl-3-methylimidazolium acetate in ethanol.

Table 2. Parameters of the hydroxypropylcellulose particles in solutions at 25ºC

Solution	R_g, nm	MM_w, g mol^{-1}	A_2, mol ml^{-1} g^{-2}
Hydroxypropylcellulose in ethanol	74	1.60×10^5	1.67×10^{-4}
Hydroxypropylcellulose in 1-ethyl-3-methylimidazolium acetate	188	7.28×10^6	4.18×10^{-6}
Hydroxypropylcellulose (extracted from IL) in ethanol	97	1.51×10^6	2.81×10^{-4}

propylcellulose aggregates and remain in them even after 7 days of dialysis. Schematically, these aggregates can be represented as in Fig. 5.

It should be mentioned that the aggregates of hydroxypropylcellulose extracted from 1-ethyl-3-methylimidazolium acetate in ethanol decompose in time: after about two weeks, separate macromolecules of hydroxypropylcellulose can be observed in the solution.

The analysis of the light scattering data allows a conclusion that the form of macromolecules of hydroxypropylcellulose in ethanol is well described by the Kashassa-Holtz model [26]: The particles of the polymer in ethanol have the wire shape. The form of macromolecules in the solution of 1-ethyl-3-methylimidazolium acetate as well as after their extraction from the ionic liquid and subsequent dissolution in ethanol cannot be described by any model may be due to the presence of the solvent in the aggregates of hydroxypropylcellulose.

The data on static light scattering for the cellulose solutions in 1-ethyl-3-methylimidazolium acetate in Guinier plots are presented in Fig. 6. As distinct from solutions of hydroxypropylcellulose, there is a large dispersion of the particle size. The molecular mass of the particles in the solution, MM_w, is 1.67×10^6 g mol^{-1}, which is one order of magnitude larger than the true molecular mass of 9×10^4 g mol^{-1}. Consequently, in the solutions of cellulose in 1-ethyl-3-methylimidazolium acetate there are no separate macromolecules of the polymer but rather their aggregates exist. The form of these aggregates is nicely described by the model of "soft spheres" (Fig. 7, black triangles).

From the data of TGA (Fig. 7) it is hard to decide whether the ionic liquid is present in these aggregates. The thermograms of the original crystalline cellulose and that precipitated from the solution in 1-ethyl-3-methylimidazolium acetate are shown in Fig. 8. A wide peak centered at ~290ºC can refer either to the decomposition of amorphous cellulose or the mixture of cellulose with the ionic liquid. Therefore, the question of the presence of the solvent in the precipitated cellulose remains open and requires further thorough investigation.

EXPERIMENTAL

For experiments, microcrystalline cellulose (Merck) with molecular mass 9×10^4 g mol^{-1} and hydroxy-

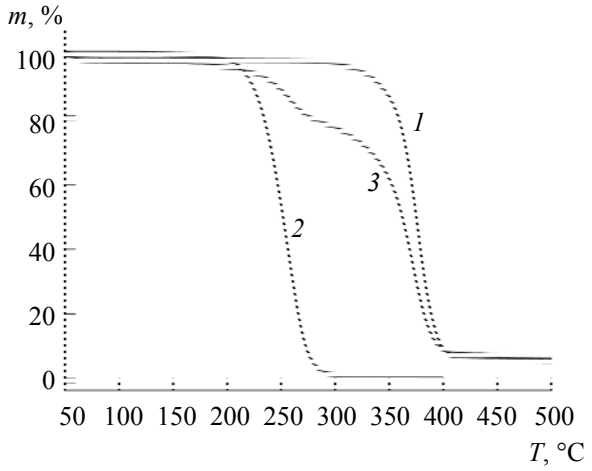

Fig. 4. TGA: (*1*) original sample of crystalline hydroxypropylcellulose; (*2*) 1-ethyl-3-methylimidazolium acetate; and (*3*) hydroxypropylcellulose extracted from 1-ethyl-3-methylimidazolium acetate.

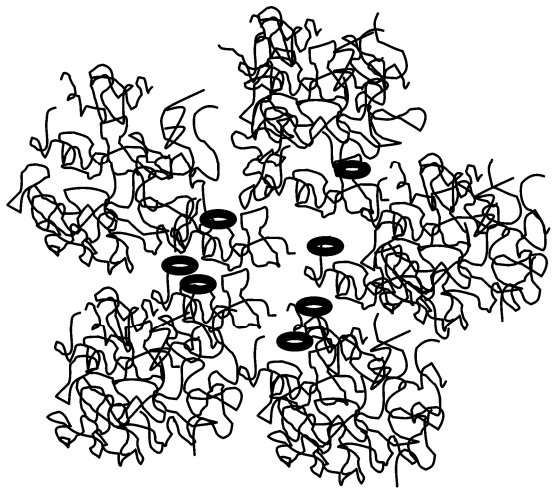

Fig. 5. Structure of aggregate of hydroxypropylcellulose with the molecules of 1-ethyl-3-methylimidazolium acetate inside.

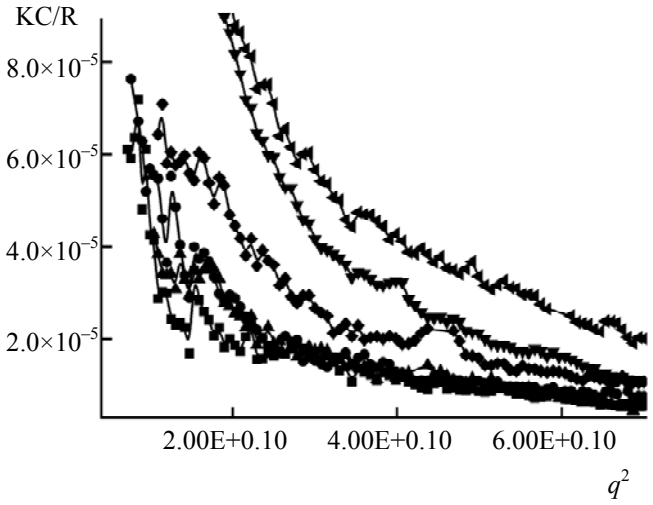

Fig. 6. Guinier plot of the data of the static light scattering for cellulose in 1-ethyl-3-methylimidazolium acetate.

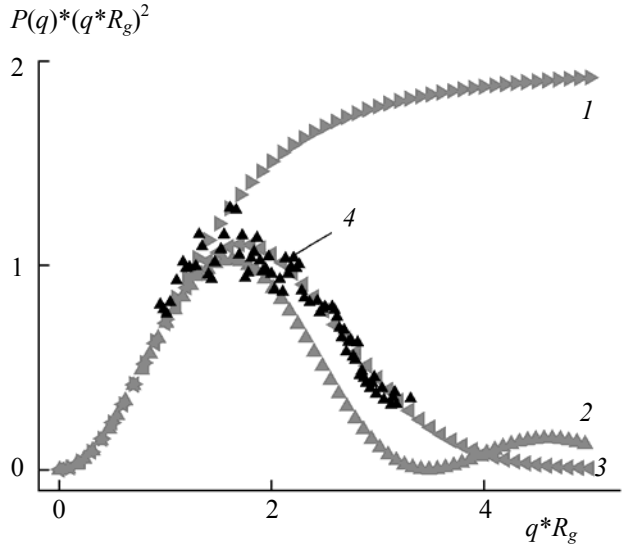

Fig. 7. Plots in the coordinates according to the Kratky procedure for the models and for cellulose in 1-ethyl-3-methylimidazolium acetate.

propylcellulose with molecular mass 1×10^5 g mol^{-1} and degree of substitution <3 were used. 1-Ethyl-3-methylimidazolium acetate (BASF) with mp < –20ºC and density 1.1027 g cm^{-3} was used as an ionic liquid, in which both studied polymers are soluble; hydroxypropylcellulose was also soluble in ethanol (Merck).

The solutions of polymers in 1-ethyl-3-methylimidazolium acetate of 0.5–5 g l^{-1} concentration were obtained by stirring at 90ºC and subsequent cooling to room temperature. The solutions of hydroxypropylcellulose in ethanol were obtained by stirring at 50ºC and subsequent cooling to room temperature. Precipitation of cellulose from its solution in 1-ethyl-3-methylimidazolium acetate was made with bidistilled water followed by thorough multiple rinsing. Since hydroxypropylcellulose is soluble in water, for its precipitation from the solution in 1-ethyl-3-methylimidazolium acetate the method of dialysis was used. The solution of hydroxypropylcellulose in 1-ethyl-3-methylimidazolium acetate was placed in a cellophane semipermeable membrane Spectra Por 1 Membrane MWCO; the solvent was removed through the membrane into bidistilled water during 7 days, water was changed no less than 12 times.

To determine the size of the particles in the solution, the method of static light scattering was used. The experiment was run on a SLS-2 Systemtechnik instrument with helium–neon laser (λ_0 = 632.6 nm) at 25ºC. The refractive indices n_0 and the increments of refractive indices of solutions of concentration c (dn/dc) were determined on a differential refractometer DR-1 (SLS Systemtecnik) at 25ºC. The thermogravimetric analysis of the samples of polymers was performed on a Mettler Toledo instrument in the range of temperatures 30–800ºC in the nitrogen atmosphere with the rate of heating 10ºC/min.

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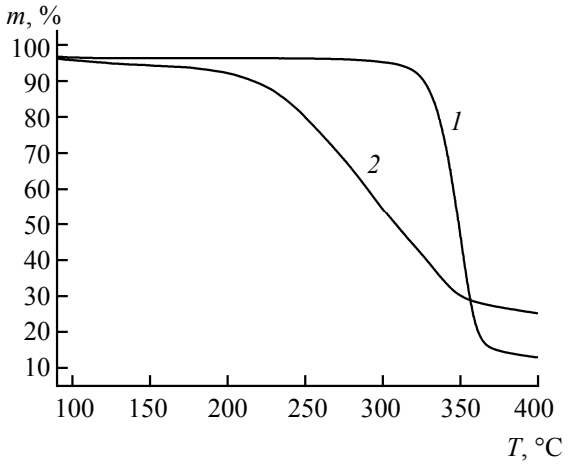

Fig. 8. TGA of cellulose: (*1*) original crystalline cellulose and (*2*) precipitated from 1-ethyl-3-methylimidazolium acetate.

REFERENCES

1. Kennedy, J.F., Philips, G.O., and Williams, P.A., *Cellulosic Pulps, Fibres, and Materials*, Abington: Woodhead Publishing Limited, 2000.
2. Bel'nikevich, N.G., Brestkin, Yu.V., Panov, Yu.N., and Frenkel', S.Ya., *Khimicheskie Volokna*, 1985, vol. 1, p. 41.
3. Iovleva, M.M., *Khimicheskie Volokna*, 1996, vol. 2, p. 11.
4. Khripunov, A.K., Plisko, E.A., Laius, L.A., Baklagina, Yu.G., Petrova, V.V., and Gerasimova, V.A., *Vysokomolek. Soed. B*, 1975, vol. 17, no. 8, p. 600.
5. Fengel, D. and Vegener, G., *Drevesina: Khimiya. Ul'trastruktura. Reaktsii* (Wood: Chemistry. Ultrastructure. Reactions), Moscow: Lesnaya Prom–t', 1988.
6. *Tsellyuloza i ee proizvodnye* (Cellulose and Its Derivatives), Baiklz, N. and Segal, L., Eds., Moscow: Mir, 1974, vols. 1, 2.
7. Kettenbach, G., Klufers, P., and Mayer, P., *Macromol. Symp*., 1997, vol. 120, p. 278.
8. Burchard, W. and Klufers, P., *Angew. Chem*., 1994, vol. 106, no. 8, p. 936.
9. Seger, B. and Burchard, W., *Macromol. Symp*., 1994, vol. 83, p. 291.
10. Schulz, L. and Burchard, W., *Papier,* 1993, no. 47, p. 1.
11. Schleicher, H., Philipp, B., and Kabrelian, V., *Papier*, 1988, vol. 42, no. 12, p. 653.
12. Nels, I., Wagenknecht, W., Philipp, B., and Stschebina, D., *Prog. Polym. Sci*., 1994, vol. 19, p. 29.
13. Volbracht, L., *Chemiefasern. Textilindustrie*, 1991, vol. 39, p. 935.
14. Heinze, T., Dicke, R., Koschella, A., Kull, A.H., Klohr, E.-A., and Koch, W., *Macromol. Chem. Phys*., 2000, vol. 201, p. 627.
15. Swatloski, R.P., Rogers, R.D., and Holbrey, J.D., Patent WO 03/029329 A3, C08J, *Dissolution and Processing of Cellulose using Ionic Liquids*, 2003.
16. Mizumo, T., *Chem. Lett*., 2004, vol. 33, no. 10, p. 1360.
17. Schulz, L., Seger, B., and Buchard, W., *Macromol. Chem. Phys*., 2000, vol. 201, no. 15, p. 2008.
18. Saalwachter, K., Buchard, W., Kettenbach, G., Klufers, P., Dugarmaa, S., and Klemm, D., *Macromolecules,* 2000, vol. 33, no. 11, p. 4094.
19. Burchard, W., Schmidt, M., and Stockmayer, W.H., *Macromolecules*, 1980, vol. 13, p. 1265.
20. Kamide, K. and Saito, M., *Adv. Polym. Sci.,* 1987, vol. 83, no. 1, p. 1.
21. Burchard, W. and Schulz, L., *Macromol. Symp*., 1995, vol. 99, no. 1, p. 57.
22. Roder, T. and Morgenstern, B., *Polymer*, 1999, vol. 40, no. 14, p. 4143.
23. Bochek, A.M., *Doctoral Sci. (Chem.) Dissertation*, St. Petersburg, 2002.
24. Drechsler, U., Radosta, S., and Vorwerg, W., *Macromol. Chem. Phys.,* 2000, vol. 201, no. 15, p. 2023.
25. Arndt, K-F., Morgenstern, B., and Rtsder, T., *Macromol. Symp*., 2002, vol. 162, p. 109.
26. Burchard, W., Sege,r B., Schulz, L., Ebringerova, A., Hromadkova, Z., Vorwerg, W., Kruger, E., and Grimm, A., *Papier*, 1994, vol. 48, no. 12, p. 755.