This article was downloaded by: [University of California, San Diego]
On: 09 August 2012, At: 14:13
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Temperature Effect on Hydrogen Bonds in Triblock Copolymers of Poly(Ethylene Oxide) and Polyacrylamide

N. M. Permyakova [a], T. B. Zheltonozhskaya [a], S. V. Fedorchuk [a], N. E. Zagdanskaya [a] & V. G. Syromyatnikov [a]

[a] Faculty of Chemistry, Macromolecular Chemistry Department, Taras Shevchenko Kyiv National University, Kyiv, Ukraine

Version of record first published: 22 Sep 2010

To cite this article: N. M. Permyakova, T. B. Zheltonozhskaya, S. V. Fedorchuk, N. E. Zagdanskaya & V. G. Syromyatnikov (2007): Temperature Effect on Hydrogen Bonds in Triblock Copolymers of Poly(Ethylene Oxide) and Polyacrylamide, Molecular Crystals and Liquid Crystals, 468:1, 53/[405]-61/[413]

To link to this article: http://dx.doi.org/10.1080/15421400701229453

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

Mol. Cryst. Liq. Cryst., Vol. 468, pp. 53/[405]–61/[413], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701229453

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

Temperature Effect on Hydrogen Bonds in Triblock Copolymers of Poly(Ethylene Oxide) and Polyacrylamide

N. M. Permyakova
T. B. Zheltonozhskaya
S. V. Fedorchuk
N. E. Zagdanskaya
V. G. Syromyatnikov
Faculty of Chemistry, Macromolecular Chemistry Department, Taras Shevchenko Kyiv National University, Kyiv, Ukraine

The existence and temperature stability of the hydrogen bond system in triblock copolymers based on chemically complementary polyacrylamide and poly(ethylene oxide) are studied. The participation of the trans*-multimers of PAA amide groups and oxygen atoms of PEO in the formation of hydrogen bonds between both polymer blocks is established. It is shown that the hydrogen bond system in the copolymers is stable enough in the wide temperature region* $T = (308 \div 473)$ *K. The insignificant destruction of the H-bonds between PAA and PEO blocks and also the* cis-trans- *and* trans*-multimers of amide groups in the triblock copolymers is revealed at the temperature increasing.*

Keywords: block copolymer; hydrogen bonds; intramolecular polycomplex; temperature

INTRODUCTION

Block and graft copolymers with strongly interacting polymer components attracted a considerable attention in recent years as multifunctional polymer materials [1–4]. They can be used as highly efficient flocculants [5,6], different binders, and polymer carriers in the drug delivery systems [7,8], as well as prospective agents of the drag reduction in turbulent flows [9,10]. It was shown that the structure and behavior of these copolymers in a solution are determined by cooperative

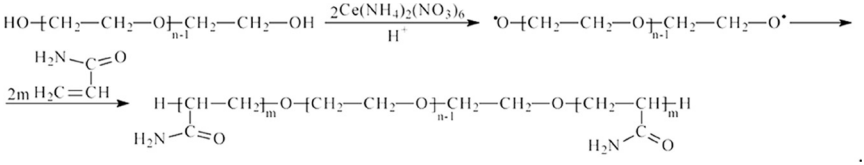
Address correspondence to N. M. Permyakova, Faculty of Chemistry, Macromolecular Chemistry Department, Taras Shevchenko Kyiv National University, 60, Volodymyrs'ka Str., Kyiv 01033, Ukraine. E-mail: permyakova@ukr.net

electrostatic interactions (in the case of the so-called ampholytic or zwitter-ion block copolymers) [1,3,4,11] or hydrogen bonds [2,7,8]. That is why such block and graft copolymers were named in our earlier work [12] as the intramolecular polycomplexes (IntraPCs).

It was established that polyacrylamide (PAA) and poly(ethylene oxide) (PEO) can interact with each other in a water solution through hydrogen bonds and can form intermolecular polycomplexes [13]. But the existence of hydrogen bonds between both polymer partners in the corresponding block copolymers was not examined. In the present work, the results of studying the hydrogen bond system in the PAA-*b*-PEO-*b*-PAA triblock copolymers comparing with individual PAA are represented. The temperature effect on the hydrogen bond stability in the copolymers is highlighted as well.

EXPERIMENTAL

Two PAA-*b*-PEO-*b*-PAA samples were synthesized at $T = 298\,\mathrm{K}$ by the free radical block copolymerization of acrylamide (AA) with poly(ethylene glycol) of different molecular weights [$M_{vPEG} = 4 \cdot 10^4$ and $1 \cdot 10^5$ from "Merk" (Germany)] which was activated by Ce^{IV} ions and used as a macroinitiator:



The PAA sample was obtained by the free radical homopolymerization of AA with the application of Ce^{IV}. The molecular characteristics of the triblock copolymers and the corresponding individual polymers are shown in Table 1.

TABLE 1 Characterization of Triblock Copolymers and Individual Polymer Components

Copolymer	$M_{vPEO} \cdot 10^{-5}$	$M_{vPAA} \cdot 10^{-5}$	$M_{v\ copolymer} \cdot 10^{-5}$	W_{PEO}[1], %
PEG	0.40	–	–	–
PAA	–	6.31	–	–
PAA-*b*-PEO-*b*-PAA1	0.40	3.18	6.76	5.9
PAA-*b*-PEO-*b*-PAA2	1.00	9.07	19.14	5.2

[1]Wt. ratio of PEO in copolymers.

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

The H-bond system between PEO and PAA in the triblock copolymers and its destruction under increasing the temperature were investigated by FTIR spectroscopy. The FTIR spectra of thin (3–7 μm) films of the triblock copolymers and individual polymer components were measured by a Nexus-470 Nicolet FTIR spectrometer (USA). The films were cast from aqueous solutions ($C = 1.5\,\mathrm{kg \cdot m^{-3}}$) on fluorite windows, air-dried, then placed under vacuum above $CaCl_2$ during one week. Their FTIR spectra were recorded in the range 1000–4000 $\mathrm{cm^{-1}}$ at 293 K. The heating of polymer films (without windows) was carried out in a thermostatted cuvette in the range of $T = (308 \div 473)$ K. The separation of the strongly overlapped vibration bands in the region of amides I and II and the determination of their positions, FWHM, and the apparent integral absorption coefficients B_i were carried out using a computer program WINSPECTRUM based on the spline method [14]. The δ_{C-H} vibration band at 1452 $\mathrm{cm^{-1}}$ was resolved well enough in the spectra and was used as a tabular line which was inscribed in a complicated contour of the overlapped bands of amides I and II.

RESULTS AND DISCUSSION

The FTIR spectra of thin polymer films for one of the triblock copolymers and individual PEG at room temperature are shown in Figure 1a,b.

It is displayed first of all, we note the 23-$\mathrm{cm^{-1}}$ low-frequency shift of the ν_{C-0-C} vibration band of PEO in the triblock copolymer spectrum

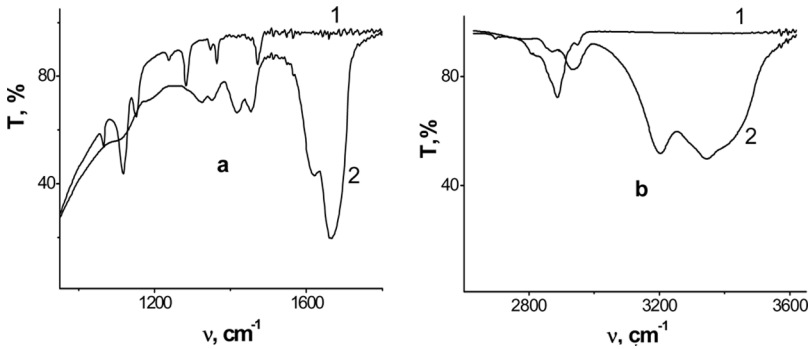


FIGURE 1 FTIR spectra of thin polymer films (on fluorite windows) of PEG-*1* and PAA-*b*-PEO-*b*-PAA2-*2* in the regions of 1000–1800 $\mathrm{cm^{-1}}$ (a) and 2600–4000 $\mathrm{cm^{-1}}$ (b). $T = 293$ K.

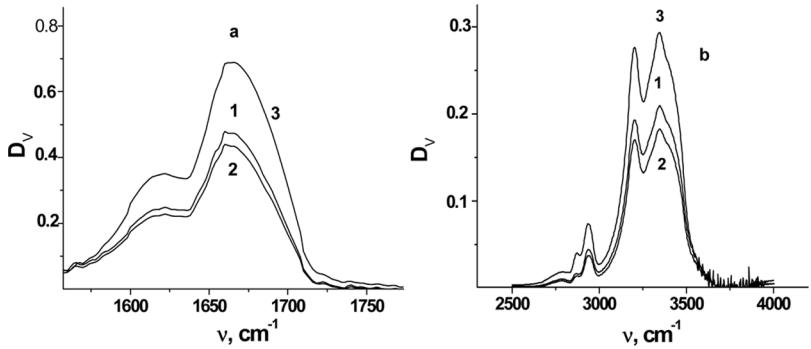


FIGURE 2 Recalculated FTIR spectra of PAA-*1*, PAA-*b*-PEO-*b*-PAA1-*2* and PAA-*b*-PEO-*b*-PAA2-*3* films in the region of amides I and II (a) and ν_{C-H}, ν_{N-H}, ν_{O-H} (b) vibrations $T = 293$ K.

(Fig. 1a, curve 2) unlike to the position of the same band in the spectrum of individual PEG at $\nu = 1113\,\text{cm}^{-1}$ (curve 1). This effect indicates the H-bond formation between the amide groups of the PAA block and oxygen atoms of the central PEO block. The results of recalculations of the FTIR spectra in two major regions taking the corresponding base lines into account are represented in Figure 2a,b.

Each spectrum in the region of amides I and II is a superposition of a great number of strongly overlapped vibration bands which correspond to various states of either free or bound amide groups. The identification of separate bands in this region for individual PAA was carefully carried out by us earlier with the help of a computer processing of the IR spectrum [15]. Basing on these data, the tabular line parameters and also the apparent positions, amplitudes, and FWHM of the bands of amides I and II in the FTIR triblock copolymer and PAA spectra were introduced into a computer. The results of the computer processing of the spectra are shown in Figure 3a,b,c.

The parameters of the separate bands of amides I and II in PAA-*b*-PEO-*b*-PAA and PAA spectra are given in Table 2.

It should be noted that the most separate vibration bands in the amide I region correspond to the different hydrogen bond structures. According to [15], there are free amide groups (structure 1), the *trans*-multimers of amide groups (structure 2), and the *cis-trans*-multimers of amide groups (structure 3). At the same time, there are also the "open dimmer" structures (structure 4) which are formed

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

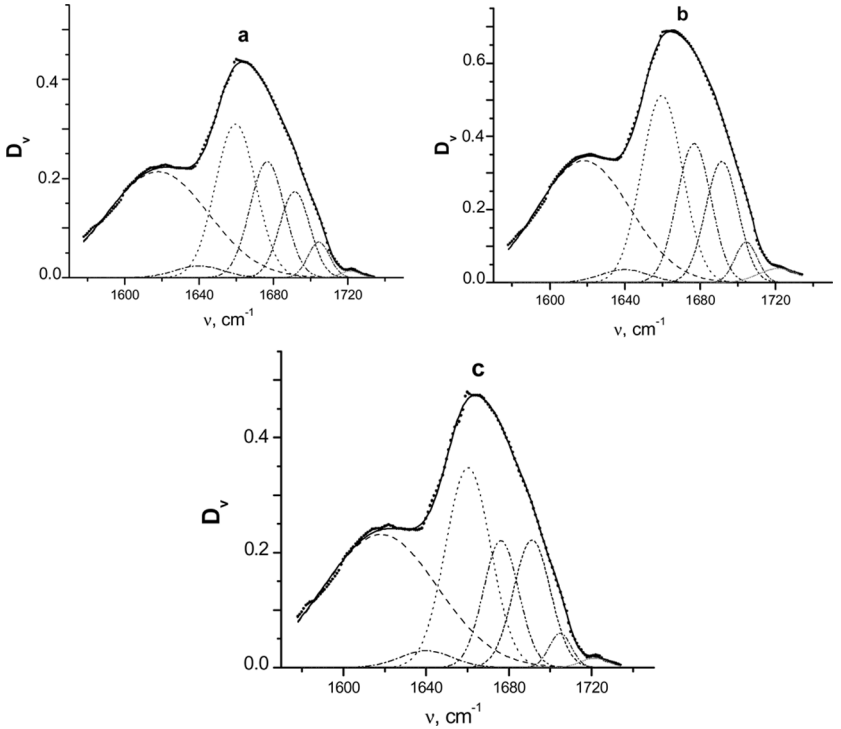
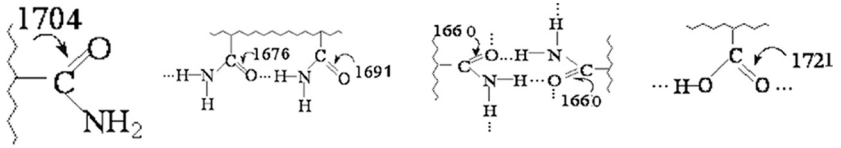


FIGURE 3 Computer processing of the FTIR spectra of PAA (a), PAA-*b*-PEO-*b*-PAA1 (b) and PAA-*b*-PEO-*b*-PAA2 (c) in the region of amides I and II. Experimental (···) and calculated (—) vibration band contours.

by an insignificant number of COOH groups contained in PAA-*b*-PEO-*b*-PAA samples.



In order to establish some alterations in the amide group distribution between different H-bond structures in the triblock copolymers comparing with PAA, the contributions of the apparent integral absorption coefficients of the amide I bands in the common amide I absorption were calculated according to the formula $\alpha_i = B_i/\sum B_i$. Such data are shown in Table 3.

TABLE 2 Parameters of the Vibration Bands of Amides I and II in PAA and PAA-*b*-PEO-*b*-PAA Films

Polymer	ν,[1] cm^{-1}	δ_ν,[2] cm^{-1}	$\Delta\nu_{1/2}$,[3] cm^{-1}	$\delta_{\Delta\nu 1/2}$, cm^{-1}	B_i,[4] cm^{-2}	δ_{Bi}, cm^{-2}	χ^2,[5] cm^{-2}
PAA	1618.1	0.2	64.4	0.5	31.75	0.21	0.3
	1640.0	1.2	29.7	3.5	1.84	0.13	0.3
	1660.3	0.2	25.6	0.3	19.00	0.15	0.3
	1676.2	0.2	20.1	0.4	9.45	0.12	0.3
	1691.2	0.2	21.0	0.3	9.91	0.12	0.3
	1704.8	0.3	12.5	0.6	1.59	0.07	0.3
	1721.3	0.5	15.6	0.9	0.54	0.03	0.3
PAA-*b*-PEO-*b*-PAA2	1617.8	0.2	62	0.6	29.02	0.20	0.2
	1639.9	1.2	30.2	4.2	1.52	0.12	0.2
	1659.6	0.2	25.7	0.3	16.95	0.15	0.2
	1676.6	0.2	21.8	0.4	10.90	0.13	0.2
	1691.4	0.1	19.0	0.3	7.04	0.11	0.2
	1704.3	0.2	16	0.4	2.10	0.04	0.2
	1721.3	0.4	12.4	0.3	0.35	0.02	0.2
PAA-*b*-PEO-*b*-PAA3	1616.0	0.2	55.8	0.4	38.32	0.22	0.3
	1638.0	0.6	30.2	2.1	4.16	0.16	0.3
	1659.6	0.1	25.7	0.2	29.10	0.18	0.3
	1676.6	0.1	21.1	0.4	17.14	0.11	0.3
	1691.4	0.1	20.5	0.2	14.68	0.14	0.3
	1704.3	0.1	14.0	0.4	3.28	0.05	0.3
	1721.3	0.5	24.7	0.9	2.04	0.05	0.3

[1]Band position.
[2]Standard deviations for corresponding values.
[3]Band half-width.
[4]Apparent integral absorption coefficient of a band.
[5]Sum of squires of deviations of all calculated points from experimental ones.

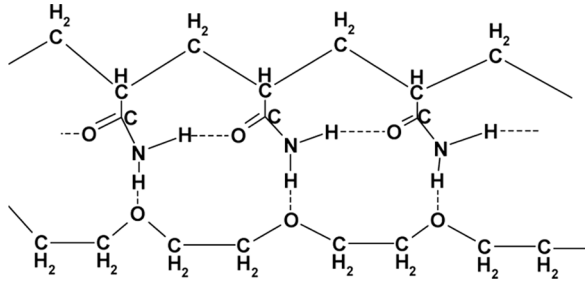
TABLE 3 Contributions of the Separated Amide I Vibration Bands in the Common $\nu_{C=O}$ Absorption for PAA-*b*-PEO-*b*-PAA and PAA

	α_i, %				
Polymer	$\nu \sim 1660$ cm^{-1}	$\nu \sim 1676$ cm^{-1}	$\nu \sim 1691$ cm^{-1}	$\nu \sim 1704$ cm^{-1}	$\beta^1 = B_{1676}/B_{1691}$
PAA	47.6	26	24.8	4.0	0.95
PAA-*b*-PEO-*b*-PAA1	45.9	29.4	19.1	5.7	1.54
PAA-*b*-PEO-*b*-PAA2	45.3	26.7	22.9	5.1	1.17

[1]Effective length of the *trans*-multimers of amide groups.

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

As seen, there is the relatively less number of the *cis-trans-* and also *trans*-associates of amide groups in the PAA-*b*-PEO-*b*-PAA films than that in individual PAA. At the same time, the effective length of the *trans*-multimers of amide groups in the block copolymers grows unlike to that in PAA. The increase of the rigidity of PAA chains in the triblock copolymers can be explained by a participation of the *trans*-multimers of amide groups in the formation of the H-bond system between PEO and PAA segments (structure 5):



5

Thus, the PAA-*b*-PEO-*b*-PAA triblock copolymers are IntraPCs whose molecular architecture is stabilized by the H-bond system between PEO and PAA blocks.

It is well known that the increasing temperature leads often to the H-bond system destruction. The temperature influence on the hydrogen bond stability in PAA-*b*-PEO-*b*-PAA1 is shown in Figure 4.

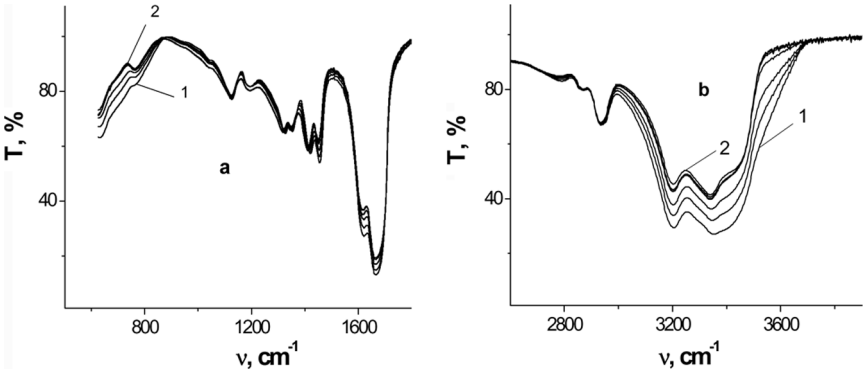


FIGURE 4 FTIR spectra of PAA-*b*-PEO-*b*-PAA1 film (without fluorite windows) under the temperature growth in the 1000–1800 cm^{-1} (a) and 2600–4000 cm^{-1} (b) regions. $T = 308$ K-*1*, $T = 473$ K-*2*.

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

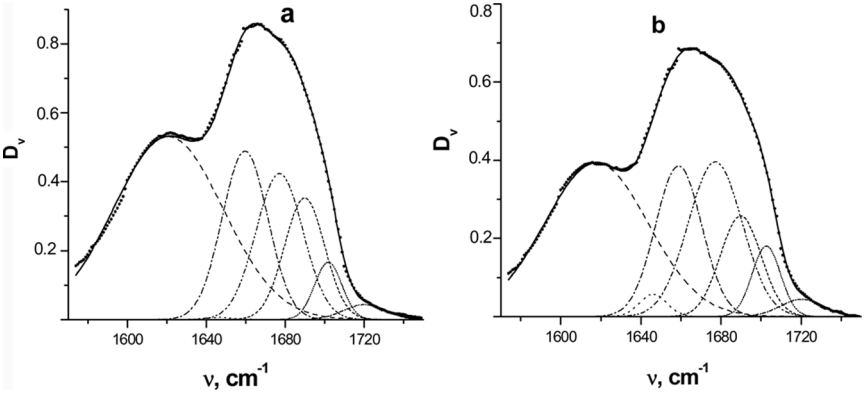


FIGURE 5 Computer processing of the FTIR spectra of PAA-*b*-PEO-*b*-PAA1 at $T = 308$ K (a) and $T = 473$ K (b) in the region of amides I and II. Experimental (···) and calculated (—) vibration band contours.

We see a certain decrease of intensities of the υ_{C-0-C}, amide I, amide II and υ_{N-H} vibration bands under increasing the temperature from $T = 308$ K (Fig. 4, curves 1) to $T = 473$ K (Fig. 4, curves 2), but the positions of these bands in the triblock copolymer spectrum are not practically changed. This fact testifies to a considerable stability of the hydrogen bond system in the copolymers in the wide temperature region. The more detailed information about the redistribution of PAA amide groups between the above-mentioned hydrogen bond structures was obtained after the computer processing of the spectral region of amides I and II at both extreme temperatures (Fig. 5, Table 4).

According to these data, the increasing temperature results in the destruction of some number of the *cis-trans*- and *trans*-multimers of amide groups with a simultaneous increase of the number of free amide groups and the effective length of *trans*-associates (Table 4).

TABLE 4 Contributions of the Separated Amide I Vibration Bands in the Common $\nu_{C=O}$ Absorption for PAA-*b*-PEO-*b*-PAA 1 at Various Temperatures

	α_i, %				
T, K	$\nu \sim 1660$ cm^{-1}	$\nu \sim 1676$ cm^{-1}	$\nu \sim 1691$ cm^{-1}	$\nu \sim 1704$ cm^{-1}	$\beta^1 = B_{1676}/B_{1691}$
308	35.9	32	22.5	7.9	1.50
473	32.5	39.0	19.2	9.3	2.03

[1]Effective length of the *trans*-multimers of amide groups.

Downloaded by [University of California, San Diego] at 14:13 09 August 2012

CONCLUSIONS

PAA-*b*-PEO-*b*-PAA triblock copolymers including chemically complementary polyacrylamide and poly(ethylene oxide) form IntraPCs stabilized by the hydrogen bond system between different polymer blocks with a participation of the *trans*-multimers of PAA amide groups and oxygen atoms of PEO.Only a small destruction of H-bonds between PAA and PEO blocks, as well as the *cis-trans*- and *trans*-multimers of amide groups in the triblock copolymers, takes place at increasing the temperature. All types of hydrogen bonds existing in the triblock copolymers demonstrate a high thermostability in the wide region from 308 to 473 K.

REFERENCES

[1] Mori, H. & Müller, A. H. E. (2003). *Prog. Polym. Sci.*, *28*, 1403.
[2] Lowman, A. M. & Peppas, N. A. (1997). *Macromolecules*, *30*, 4959.
[3] Gohy, J.-F., Creutz, S., Garcia, M., Mahltig, B., Stamm, M., & Jerôme, R. (2000). *Macromolecules*, *33*, 6378.
[4] Shibanuma, T., Aoki, T., Samui, K., Ogata, N., Kikuchi, A., Sakurai, Y., & Okano, T. (2000). *Macromolecules*, *33*, 444.
[5] Deshmukh, S. R. & Sing, R. P. (1986). *J. Appl. Polym. Sci.*, *32*, 6133.
[6] *Ukrainian Pat*. 29933, Promislova vlastnist' (3) (2002).
[7] Peppas, N. A. & Klier, J. J. (1991). *Controll. Release*, *16*, 203.
[8] Bromberg, L. (1998). *J. Phys. Chem. B*., *102*, 1956.
[9] Ungeheuer, S., Bewersdorff, H.-W., & Sing, R. P. (1989). *J. Appl. Polym. Sci.*, *37*, 2933.
[10] Mel'nik, N. P., Zheltonozhskaya, T. B., Momot, L. N., Uskov, I. A., & Matveenko, M. M. (1990). *Ukr. Khim. Zh.*, *56*, 539.
[11] Goloub, T., de Keizer, A., & Cohen Stuart, M. A. (1999). *Macromolecules*, *32*, 8441.
[12] Zheltonozhskaya, T. B., Zagdanskaya, N. E., Demchenko, O. V., Momot, L. N., Permyakova, N. M., Syromyatnikov, V. G., & Kunitskaya, L. R. (2004). *Russian Chemical Reviews*, *73*(8), 813.
[13] Momot, L., Zheltonozhskaya, T., Permyakova, N., Fedorchuk, S., & Syromyatnikov, V. (2005). *Macromol. Symp.*, *222*(1), 209.
[14] Nurberger, G. (1989). *Approximation by Spline Function*, Springer Verlag: Berlin, 243.
[15] Permyakova, N., Zheltonozhskaya, T., Demchenko, O., Momot, L., Filipchenko, S., Zagdanskaya, N., & Syromyatnikov, V. (2002). *Polish J. Chem*., *76*, 1347.

Downloaded by [University of California, San Diego] at 14:13 09 August 2012