Polish J. Chem., **78**, 1039–1046 (2004)

Synthesis of Block and Random Copolymers of Isoprene *via* Two-Electron Transfer Mechanism*

by H. Janeczek and Z. Jedliński**

Polish Academy of Sciences, Centre of Polymer Chemistry,
34, M.Curie-Skłodowska St., 41-800 Zabrze, Poland

(Received March 29th, 2004)

Supramolecular complexes of alkali metals, capable of two electron transfer and generation of carbanions have been utilized in the polymerization of isoprene. The "living" polyisoprene blocks were subsequently used to react with styrene to produce the relevant block copolymers. The polyisoprene-polystyrene random copolymers were also obtained. The novel type of anionic polymerization initiated *via* novel supramolecular catalyst yields polyisoprene copolymers with well defined structure and properties.

Key words: anionic polymerization, copolymers of isoprene, two-electron transfer, polyisoprene-polystyrene copolymers

Isoprene is well known monomer of great importance in industrial processes. Its polymers were first used for synthetic rubber production in 1917 and are still of interest because of theirs good mechanical and thermomechanical properties [1], and excellent weatherability.

The metallic sodium and potassium were first used as initiators of isoprene polymerization by Matthews and Strange [2], and Harries [3,4]. Ziegler and coworkers [5–7] used lithium, sodium or alkyllithium species in reactions with dienes, *e.g*. isoprene and butadiene. Studies of isoprene polymerization with metallic lithium [8] and rubidium [9], metallic cesium and its compounds [10] used as initiator, in hydrocarbons and etheral solvents or in bulk, were also published.

The polymerization with lithium alkyls used as initiators yields predominantly *cis*-1,4-polyisoprene in either bulk or solution polymerization [11–17], however 3,4 polymer was obtained in the polymerization of isoprene by lithium alkyls in ether solvents, or in presence of small amounts of a THF [13,18,19]. The influence of cation size (Li, Na, K, Cs) and temperature on polymer microstructure in polymerization of isoprene by these metal alkyls in benzene was discussed [20]. Although polymerization of these monomers using traditional initiators is very well known the research on isoprene polymerization is still alive. Nowadays various novel catalysts as metallorganic-metallocene catalysts are also used [21–23]. Szwarc and coworkers showed that sodium naphthalenide was capable of initiating polymerization of styrene, butadiene and isoprene *via* one electron transfer mechanism [24].

---

* Dedicated to Prof. E. Borowski on the occasion of his 75th birthday.

** Author to whom correspondence should be addressed; E-mail: jedlinski.zbigniew@cchp-pan.zabrze.pl

The discovery of crown ethers by Pedersen [25] and cryptands by Lehn [26] capable of complexing alkali metal cations provided new opportunities in organic synthesis [27].

It has been demonstrated, that alkali metals such as potassium and sodium can be dissolved to form blue metal solutions in aprotic ethereal solvents, *e.g.* tetrahydrofuran after addition of a crown ether [28].

Such solutions have been used by Schue and coworkers [29–31] as initiators of isoprene polymerization. However, composition of such solution was not precisely defined and polymerization results were not well reproducible. The studies of metal dissolution enable preparation of well defined metal solutions containing alkali metal ion pairs and only negligible concentration of electrons [32,33]. The main active species in such solutions are alkali metal ion pairs, *e.g.* K^+L,K^-, accordingly to the equation:

$$2M(s) + L \rightarrow M^+L + M^-$$

where M is the alkali metal, *e.g.* potassium or sodium, and L is a complexant, *e.g.*, 18-crown-6. Such alkali metal ion pairs: M^+L,M^- are able to transfer two electrons towards a suitable substrate to form a carbanion:

$$M^+L,M^- \xrightarrow[\text{transfer of 2 electrons}]{\text{substrate (electrophile)}} M^+L + \text{carbanion} \qquad (1)$$

It is a general reaction proceeding with electrophiles which are able to accept two electrons and become carbanions.

If an electrophile is added in excess to reaction medium, a carbanion formed at the first step (eq. 1) is able to react with the added substrate and initiate the polymerization to form a polymer. In the previous papers we demonstrated the polymerization of many monomers as styrene [34,35], methyl methacrylate [36,37], alkyl halides [38], silyl halides [39], isoprene [40] as well as in the ring opening polymerization of lactones [41–43] and oxiranes [44].

In this paper we report on the synthesis of isoprene copolymers with styrene using this novel catalyst inducing two-electron transfer. Isoprene copolymers were previously obtained using anionic [45–50], cationic [51], coordination [52], radical polymerization [53] techniques and also radical polymerization techniques with metallocene catalysts [45]. Such copolymers are of interest because they may be used for rubber production, and as effective compatibilizers for rubber blends, and in medicine as material for potential prosthetic applications [53,54].

The presented process proceeding *via* two electron transfer mechanism [40] enables synthesis of isoprene copolymers with desired structure having no traces of catalysts and metals. It is a great advantage of these catalysts if compared with previously described conventional catalyst systems.

EXPERIMENTAL

Materials. Isoprene (Aldrich) was dried over calcium hydride and then distilled under argon before use. 18-crown-6 was purified as described previously [31,32]. THF was purified as described previously [55] and then distilled over a sodium-potassium alloy in atmosphere of dry argon. Styrene (from Fluka) before polymerization was freshly distilled at a reduced pressure after drying over calcium hydride. The fraction boiling at 63°C (60 mm Hg) was collected. Methanol (commercial grade from POCh) was used as received.

Preparation of the initiator. The 0.03 mol/l THF solution of supramolecular complex of potassium was obtained by the contact of the potassium mirror with a solution of 18-crown-6 in THF (0.03 mol/l) for 15 min at the temperature 10°C under inert gas atmosphere. The dissolved potassium forms potassium complex consisting of potassium ion pairs: K^+crown,K^-. After 15 min the resulting blue mixture was filtered through a coarse frit to the thermostated glass reactor.

Polymerization. *Block copolymerization of isoprene with styrene.* The first step for preparing PI-PST block copolymers was a homopolymerization of isoprene. The polymerization was conducted in THF at 10°C. A calculated amount of the solution of an initiator–supramolecular potassium complex was introduced into the thermostated glass reaction chamber and next the solution of isoprene in THF was slowly added. After *ca.* 5 minutes, a styrene solution of suitable concentration was added slowly to the solution containing living polyisoprene. After completion of polymerization (5–10 min) the copolymer was precipitated in cold methanol and filtered off. The precipitate was washed with methanol several times and dried under vacuum. The polymer was kept in darkness at –10°C. The results of polymerization are presented in Table 1. Copolymer composition, depending on the ratio of isoprene, was estimated from ^{1}H NMR.

Random copolymerization of isoprene with styrene. The polymerization was conducted in THF at 10°C. A calculated amount of the solution of an initiator was introduced into the thermostated glass reaction chamber and next the solution containing mixture of isoprene and styrene in THF was slowly added. After completion of polymerization (5 min) the copolymer was precipitated in cold methanol and filtered off. The precipitate was washed with methanol several times and dried under vacuum. The polymer was kept in darkness at –10°C. The results of polymerization are presented in Table 2. Copolymer compositions, depending on the ratio of isoprene, was estimated from ^{1}H NMR.

Measurements. The percentage yields of copolymers were determined by weighing the dried polymer. Number average molecular weights were determined by VPO technique in $CHCl_3$ using Knauer vapour pressure osmometer and by Gel Permeation Chromatography (GPC). The molecular weight and polydispersity of both the polyisoprene and the block copolymers were determined by GPC according to polyisoprene standards with low polydispersity and similar microstructure (Polymer Source Inc.). GPC experiments were conducted in THF at 35°C, using the Spectra-Physics 8800 gel permeation chromatograph. The structure of copolymers was analyzed by ^{1}H NMR spectroscopy, using a Varian VXR-300 Multinuclear spectrometer. The polymer solutions for measurements were prepared by dissolving *ca*. 50 mg copolymer in about 3 ml of deuterated chloroform ($CDC1_3$).

The glass transition temperature (T_g) of polymer samples was determined by differential scanning calorimetry (DSC 2010 TAinstrument), calibrated with indium and gallium. Samples were heated at 140°C, cooled rapidly to –70°C, and then reheated at 20°C/min to 130°C.

RESULTS AND DISCUSSION

It was found previously that polymerization of isoprene initiated by supramolecular complex of potassium proceeds *via* two-electron transfer mechanism [40]. In the reaction of isoprene with alkali metal complex two electrons are transferred from the initiator to the isoprene monomer to form dianion, which undergoes instant

protonation by the solvent and yields a respective isoprene carbanion which is capable of inducing isoprene polymerization (Scheme 1). The "living" character of this process allowed the copolymerization with styrene. For simplicity only one resonance form of a radical anion and dianion are depicted on this Scheme. The results of isoprene copolymerization with styrene initiated with K^-/K^+18C6 complex in THF are shown in Tables 1–2.

Scheme 1

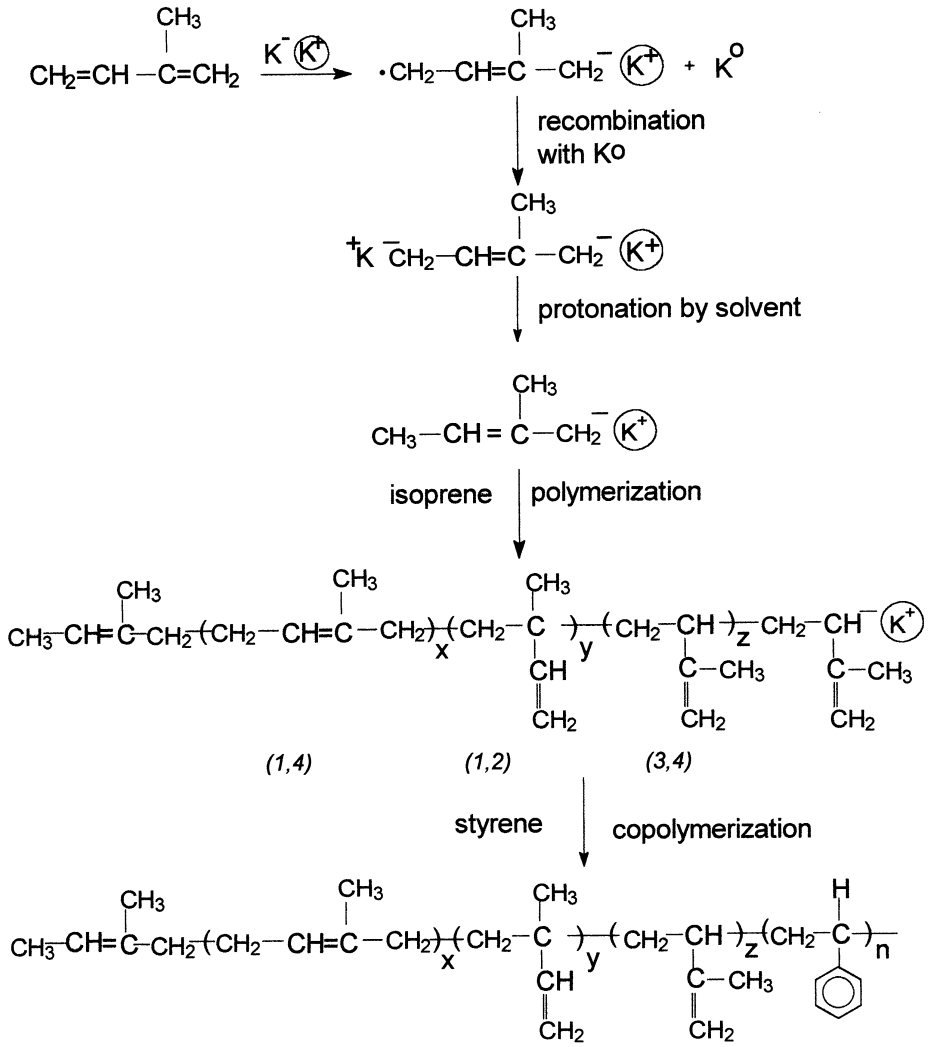

Figure 1 shows a ^{1}H-NMR spectrum of the synthesized block copolymer.

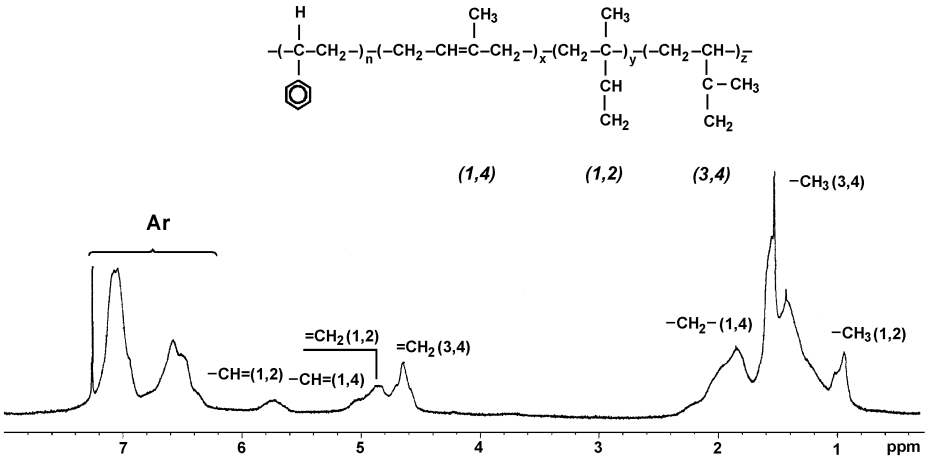

Figure 1. The ^{1}H NMR (300 MHz) spectrum of polyisoprene-polystyrene block copolymer (M_n = 31600; PI = 1.8), obtained in the presence of supramolecular complex of potassium in THF, at 10°C.

The analysis of the polyisoprene-poly(styrene) block copolymer ^{1}H NMR spectra [56] (Figure 1) indicates, that the polymerization leads to polymer containing *ca*. 37% (1,4); 34% (3,4) and 29% (1,2) chain structures.

It was found that the block copolymerization of isoprene with styrene and random copolymerization of isoprene with styrene initiated by supramolecular complex of potassium in THF proceeds fast at room temperatures. The copolymers obtained exhibit high molecular weights (Table 1 and 2). Polydispersities of synthesized polymers were considerably high (1.2–1.8). This is possibly due to the fact that a bimolecular termination is not totally prevented. This effect is probably also due to the increased temperature and the high exothermic effect in viscose medium of the reaction. Therefore, this way is considered to be a non-truly living mechanism. Nevertheless, for some applications where the level of polydispersity is not crucial, it is a suitable technique that can be used for preparation of such copolymers.

Table 1. Properties of block copolymers of isoprene and styrene obtained *via* polymerization initiated by K^-/K^+, 18C6 complex at 10°C.

No	Yield (%)	10^{-3} M_n (exp)[d]	M_w/M_n	Polymer Compos[a]. (%) Isoprene	T_g[b] (°C)	T_g[c] (°C)
1	100	10.00	1.3	75	3.6	101
2	100	29.41	1.4	55	–3.7	100.2
3	100	18.89	1.4	32	1.8	101.2
4	100	31.60	1.8	21	–2.7	97.5
5	100	30.20	1.6	9	–1.8	99.2

[a] Estimated from ^{1}H-NMR.
Heating rate – 20 deg/min; T_g, for: [b] polyisoprene block, [c] polystyrene block.
[d] Estimated by GPC using polyisoprene standards with low polydispersity (Polymer Source Inc.).

Table 2. Properties of random copolymers of isoprene and styrene obtained *via* polymerization initiated by K^-/K^+, 18C6 complex at 10°C.

No	Yield (%)	10^{-3} M_n (exp)[c]	M_w/M_n	Polymer Compos[a]. (%) Isoprene	T_g[b] (°C)
1	100	21.53	1.4	72	15.2
2	100	21.57	1.6	52	39.1
3	100	38.14	1.5	44	38.2
4	100	5.38	1.2	20	53.2

[a] Estimated from ^{1}H-NMR.
[b] Heating rate – 20 deg/min.
[c] Estimated by GPC using polyisoprene standards with low polydispersity (Polymer Source Inc.).

The block and random copolymerization of isoprene with styrene with K^-/K^+, 18C6 complexes as initiator yields polymers showing the unimodal MWD (Figure 2). All obtained copolymer samples were amorphous (Table 1 and 2).

Results of selective extraction, ^{1}H NMR spectra, GPC and DSC revealed that the polyisoprene-poly(styrene) block and random copolymers could be obtained. The DSC studies of block copolymers showed the glass transitions of polystyrene and polyisoprene main chains (Table 1).

CONCLUSIONS

The anionic copolymerization of isoprene with styrene, in the presence of novel initiator – supramolecular complex of potassium with 18-crown-6 in THF (K^-/K^+, 18C6), can be used in random or block copolymerization. The described supramolecular catalyst is extremely convenient because it works perfectly at room temperature yielding polymers with high molecular weights and with not very broad polydispersity (1.2–1.8). The ^{1}H NMR have been used to control the structure of the

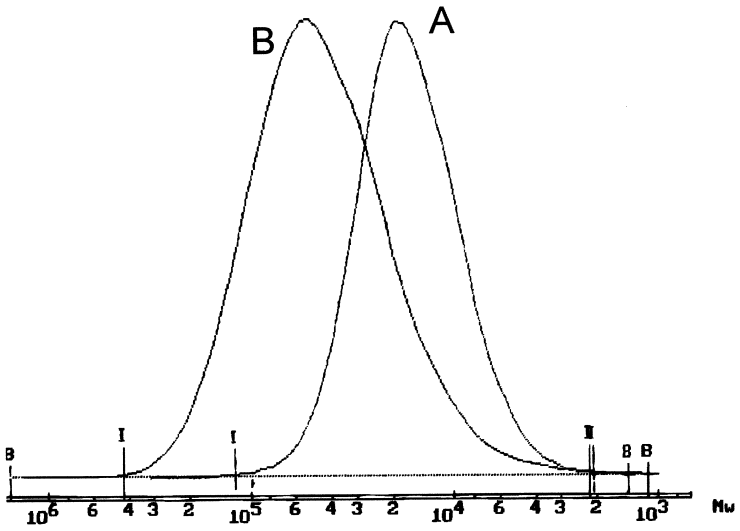

Figure 2. Overlaid GPC traces of: (**A**) – polyisoprene prepolymer prepared with supramolecular complex of potassium in THF at 10°C (M_n = 11800; PI = 1.5) and (**B**) – corresponding polyisoprene-polystyrene block copolymer (M_n = 31600; PI = 1.8).

resulting copolymers and the estimated microstructure of synthesized polyisoprene blocks contain: 37% (1,4); 34% (3,4) and 29% (1,2) structures respectively. The "living" character of the polymerization provides opportunity of synthesis of polyisoprene and its well defined copolymers with styrene.

Acknowledgment

The financial support from the Polish State Committee for Scientific Research (Grant PBZ-KBN 15/T09/99/01a) is acknowledged.

REFERENCES

1. Schoenberg E., Marsh H.A., Walters S.J. and Saltman W.M., *Rubber Chem.Technol*., **52**, 526 (1979).
2. Matthews F.E. and Strange E.H., Brit. Pat. 24 790 (1910).
3. Harries C.H., *Ann.,* **383**, 157 (1911).
4. Harries C.H., U.S. Pat. 1 058 056 (1913).
5. Ziegler K., Dersch F. and Willthan H., *Ann.,* **511**, 13 (1934).
6. Ziegler K. and Jakob L., *Ann.,* **511**, 45 (1934).
7. Ziegler K., Jakob L., Willthan H. and Wenz A., *Ann.,* **511**, 64 (1934).
8. Tobolsky A.V. and Rogers C.E., *J. Polymer Sci*., **40**, 73 (1959).
9. Frank C.E. and Foster W.E., *J. Org. Chem*., **26**, 303 (1961).
10. Rembaum A., Elis F.R., Morrow R.C. and Tobolsky A.V., *J. Polymer Sci*., **61**, 155 (1962).
11. Stavely F.W., *Ind. Eng. Chem.,* 48, 778 (1956).
12. Kuntz I., *J. Polym. Sci.,* **A2**, 2827 (1962).

13. Stearns R.S. and Forman L.E., *J. Polym. Sci.,* **16**, 381 (1959).
14. Schue F., Worsfold D.J. and Bywater S., *Polym. Letters,* **7**, 821 (1969).
15. Sledz J., Kaempf B. and Schue F., *Makromol. Chem*., **176**, 459 (1975).
16. Schue F., Worsfold D.J. and Bywater S., *Macromolecules,* **3**, 509 (1970).
17. Worsfold D.J. and Bywater S., *Macromolecules,* **5**, 393 (1972).
18. Hsieh H., Kelley D.J. and Tobolsky A.V., *J. Polym. Sci*., **26**, 240 (1957).
19. Hsieh H. and Tobolsky A.V., *J. Polym. Sci*., **26**, 245 (1957).
20. Salle R., Essel A., Gole J. and Pham Q.T., *J. Poly. Science, Polym. Chem*., **13**, 1855 (1975).
21. Barbotin F., Monteil V., Llauro M.F., Boisson C. and Spitz R., *Macromolecules,* **14**, 8521 (2000).
22. Batis Ch., Karanikolopoulos G., Pitsikalis M. and Hadjichristidis N., *Macromolecules,* **33**, 8925 (2000).
23. Dong W.M. and Masuda T., *J. Polym. Sci., Part A: Polym.Chem.*, **40**, 1838 (2002).
24. Brody H., Ladacki M., Milkovitch R. and Szwarc M., *J. Polym. Sci*., **25**, 221 (1957).
25. Pedersen C.J., *J. Am. Chem. Soc.,* **89**, 2495 (1967).
26. Lehn J.M., *Structure and Bonding,* **16**, 1 (1974).
27. Jedliński Z., *Acc. Chem. Res.*, **31**, 55 (1998).
28. Dye J.L., *J. Phys. IV,* **C5***,* 259 (1991).
29. Boileau S., Keampf B., Lehn J.M. and Schue F., *J. Polym. Sci., Polym. Lett. Ed.,* **12**, 203 (1974).
30. Boileau S., Keampf B., Raynal S., Lacoste J. and Schue F., *J. Polym. Sci., Polym. Lett. Ed.,* **12**, 211 (1974).
31. Alev S., Schue F. and Kaempf B., *J. Polym. Sci., Polym. Lett. Ed.,* **15**, 397 (1975).
32. Jedliński Z., Stolarzewicz A., Grobelny Z. and Szwarc M., *J. Phys. Chem.*, **88***,* 6094 (1984).
33. Jedliński Z. and Sokół M., *J. Pure Appl. Chem.,* **67***,* 587 (1995).
34. Jedliński Z., Czech A., Janeczek H. and Kowalczuk M., *J. Am. Chem. Soc*., **117**, 8678 (1995).
35. Szwarc M., Janeczek H. and Jedliński Z., *Macromolecules,* **30**, 4498 (1997).
36. Jedliński Z., Janeczek H. and Bosek I., *J. Org. Chem.*, **64**, 4956 (1999).
37. Janeczek H., Jedliński Z. and Bosek I., *Macromolecules,* **32**, 4503 (1999).
38. Jedliński Z., Janeczek H., Matuszowicz A. and Grobelny J., *Macromol. Rapid Commun.,* **18**, 529 (1997).
39. Jedliński Z., Kurcok P. and Nozirow F., *Macromol. Rapid. Commun*., **18**, 483 (1997).
40. Janeczek H. and Jedliński Z., *Polymer,* **43**, 7219 (2002).
41. Jedliński Z., *Pure Appl. Chem.,* **65**, 483 (1993).
42. Jedliński Z., Kowalczuk M. and Misiołek A., *J. Chem. Soc., Chem.Commun.,* 126 (1998).
43. Jedliński Z., Misiołek A. and Kurcok P., *J. Org. Chem.,* **54**, 1500 (1989).
44. Janeczek H. and Jedliński Z., *Polish Journal of Applied Chemistry*, XLI, **4**, 377 (1997).
45. Markel E.J., Weng W., Peacock A.J. and Dekmezian A.H., *Macromolecules,* **33**, 8541 (2000).
46. Takano A., Kondo K., Ueno M., Ito K., Kawahara S., Isono Y., Suzuki J. and Matsushita Y., *Polymer J.*, **33**, 732 (2001).
47. Hou S. and Chan W.K., *Macromolecules,* **35**, 850 (2002).
48. Avgeropoulos A., Paraskeva S., Hadjichristidis N. and Thomas E.L., *Macromolecules,* **35**, 4030 (2002).
49. Pantazis D., Schulz D.N. and Hadjichristidis N., *J. Polym. Sci., Part A:Polym. Chem.* **40**, 1476 (2002).
50. Mayumi H., *Int. Symp. on Ionic Polymerization,* Boston, June **30**, 2003.
51. Donderer M., Langstein G., Schafer M. and Nuyken O., *Polym. Bull*., **47**, 509 (2002).
52. Zhang Q.S., Ni X.F., Zhang Y.F. and Shen Z.Q., *Macromol. Rapid. Commun.,* **22**, 1493 (2001).
53. Wootthikanokkhan J., Peesan M. and Phinyocheep P., *Europ. Polym. J*., **37**, 2063 (2001).
54. Nazhat S.N., Parker S., Patel M.P. and Braden M., *Biomaterials*, **22**, 2411 (2001).
55. Weissberger W., Organic Solvents, Wiley, New York 1970, p. 704.
56. Morton M. and Fetters L.J., *Rubber Chem. Technol*., **48**, 359 (1979).