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Synthesis of a graft polymer PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] in “one-step” by radical/cationic transformation polymerization and coupling reaction

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ABSTRACT

This article reports a new “one-step” synthesis of graft polymers based on the radical/cationic transformation polymerization. Using the synthetic method proposed, a graft polymer (PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO]) consisting of a partly hydrolyzed poly(vinyl acetate) (PVAc-OH) backbone and block polymer grafts of acrylonitrile/*n*-butyl vinyl ether random copolymer (P(AN-*r*-BVE)) and poly(cyclohexene oxide) (PCHO) was synthesized *in situ* by radical/cationic transformation polymerization of a mixture of AN/BVE/CHO in the presence of PVAc-OH. The graft polymer, PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO], was fully characterized by ^{1}H NMR, IR, gel permeation chromatography and differential scanning calorimetry. The graft polymer, PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO], was hydrolyzed with NaOH to form a poly(vinyl alcohol)-based amphiphilic graft polymer, PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO]. The aggregation behavior of the amphiphilic graft polymer was investigated briefly by atomic force microscopy and dynamic light scattering measurements.

1. Introduction

Graft polymers have been widely used as macromolecular materials such as surfactants in composite materials [1–5] and drug delivery system [6,7] because of their unique properties due to modifications of linear conventional polymers. Thus, there have been a number of papers on synthesis of graft polymers [8–11]. Especially, recent developments of living polymerization techniques have expanded the type of monomers to be employed for the synthesis of graft polymers [12–15]. Syntheses of graft polymers are mainly classified into the following three methods: “grafting-through” [16–18], “grafting-from” [19–21] and “grafting-to” [22–24] methods. These methods generally require multiple steps.

Apart from living polymerization techniques, syntheses of new types of block polymers with well-designed architecture have been challenged from the points of new development of conventional polymers. Radical promoted cationic polymerization and transformation polymerization have been performed as ways to get block polymers [25–29].

We have independently synthesized several block copolymers by radical/cationic transformation polymerization in the extension of ESR study on radical polymerization [30–33]. In radical/cationic transformation polymerization, (1) monomer A is first polymerized by radical mechanism, (2) an electron transfers from the propagating radical of polymer of monomer A to an electron acceptor to form the corresponding polymeric cation, and (3) the polymeric cation initiates cationic polymerization of monomer B. Radical/cationic transformation polymerization allows one to synthesize unique block copolymers composed of blocks of poly(vinyl monomers) and poly(ethers). If the propagating cations coupled with a linear polymer *in situ*, graft polymers would be formed in “one-step”.

In this study, we employed block polymer of acrylonitrile/*n*-butyl vinyl ether random copolymer (P(AN-*r*-BVE)) and poly(cyclohexene oxide) (PCHO) as grafts and a partly hydrolyzed poly(vinyl acetate) (PVAc-OH) as the polymer backbone because the grafts with three different monomer units can modify the thermo-property and amphiphilic property of PVAc at a very wide range. This article reports a new “one-step” synthesis of a graft polymer, PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO], based on radical/cationic transformation polymerization of a mixture of AN/BVE/CHO in the presence of PVAc-OH (Scheme 1). Furthermore, the graft polymer obtained is hydrolyzed to form a poly(vinyl alcohol)-based amphiphilic graft polymer and its aggregation behavior is also described.

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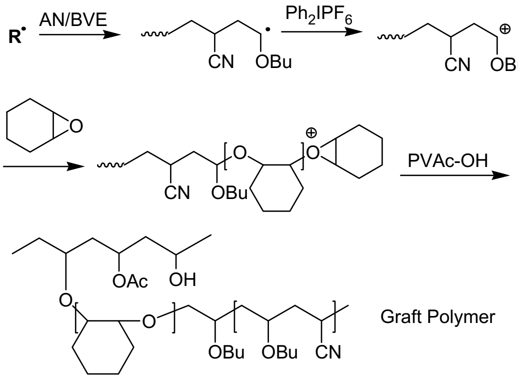

Scheme 1. Schematic representation for the radical/cationic transformation polymerization and the coupling reaction with PVAc-OH to form the graft polymers.

2. Experimental section

2.1. Materials

Commercially available 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Diphenyliodonium hexafluorophosphate (Ph_2IPF_6) (Sigma–Aldrich Chemical Co.) was used without further purification. Commercially available acrylonitrile (AN), dichloroethane, *n*-butyl vinyl ether (BVE) and cyclohexene oxide (CHO) (Acros Chemical Co.) were dried over calcium hydride, and distilled under reduced pressure prior to use. A partly hydrolyzed poly(vinyl acetate) (PVAc-OH), whose degrees of polymerization and hydrolysis were 220 and 16%, respectively, was provided by Kuraray Company.

2.2. Synthesis of a graft polymer

A dichloroethane solution of a given amount of AIBN, Ph_2IPF_6, monomers and a partly hydrolyzed PVAc in a glass ampoule was degassed by three freeze–thaw–pump cycles. The ampoule was sealed under high vacuum, and kept at a predetermined temperature in the dark. After predetermined time, the ampoule was opened and then the content was poured into an excess of hexane to give a precipitate. The precipitate was further purified to obtain the graft copolymers. An example for the synthesis is given in Table 1 and the separation procedure is shown in Fig. 1.

The polymer solution of run 5 in Table 1 was added to 25 mL of hexane to give a white precipitate. The precipitate was separated by centrifugation. The supernatant liquor was concentrated, resolved in THF and poured into excess of methanol to give a polymer of Part A containing no PVAc-OH. The precipitate in hexane was resolved in THF and poured into 25 mL of a mixture of methanol/water (5/4, v/v). The insoluble fraction was dried and characterized as the graft polymers (Part B) in 76% (w) of the total polymers of run 5. The soluble fraction was concentrated to give Part C that was reprecipitated from 1,2-dichloroethane and *n*-hexane system.

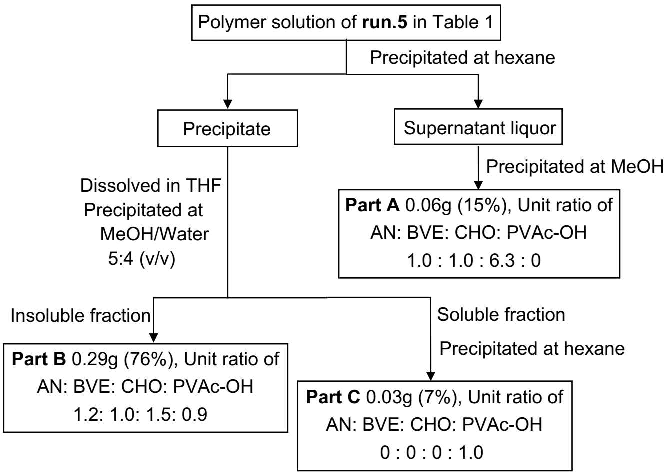

Fig. 1. Separation procedure for the graft copolymers.

2.3. Hydrolysis of the graft polymer

The graft polymer obtained (0.2 g) was dissolved in tetrahydrofuran (THF) (10 mL). A solution of NaOH in methanol (10%, 2 mL) was added to the solution. The reaction mixture was stirred and warmed at 50 °C. After 2 h, the graft polymer was recovered by precipitation using methanol with 95% yield.

2.4. Characterizations

^1H NMR spectra were measured on a Varian 300M spectrometer. Gel permeation chromatography (GPC) measurements were made on a Waters system, which consisted of a Water 515 HPLC pump, a Water 2410 refractive index detector, and Water styragel HT2, HT3, and HT4 columns connected in a series, using THF as eluent at a flow rate of 1.0 mL/min. Molecular weights were calibrated by polystyrene standards (water company standard product). FT-IR measurements were performed using a Magna-IR 750 (Nicolet Company, American) by the microscope-infrared spectroscopy method. DSC spectra for the polymers were measured on a Dupont 1090B, at a heating rate of 10 °C/min under a slow stream of nitrogen (Fig. 2). Light scattering measurements were performed using an ALV/CGS-5022F (ALV/Laser Vertriebsgesellschaft m.b.H Company, Germany) apparatus at 25.00 ± 0.01 °C, consisting of an automatic goniometer table and

Table 1
Radical/cationic transformation polymerizations of AN/BVE/CHO and coupling reaction of the end cations of the block polymers with PVAc-OH.

Run	AIBN, mM	Ph_2IPF_6, mM	PVAc-OH, g/2 mL	Yield,[a] %	M_n, 10^4	M_w/M_n, 10^4	Comonomer unit ratio in the polymer obtained[b] (AN:BVE:CHO:PVAc-OH)
1	12	0	0	44	2.6	–	1.3:1.0:0.0:0.0
2	12	0	0.1	47	–	–	1.2:1.0:0.0:0.0
3	12	24	0	28[c]	2.1	2.0	1.2:1.0:1.4:0.0
4	0	24	0.1	3.0	–	–	0.0:0.1:1.0:0.0
5	12	24	0.1	44[c]	4.2[d]	2.1	1.2:1.0:1.5:0.90[d]

The concentrations of AN, BVE, and CHO were fixed at 0.6, 1.5, and 2.5 M, respectively. The polymerization was carried out at 80 °C for 4 h. The polymer obtained was recovered by precipitation using methanol. PVAc-OH is soluble in methanol.

[a] The yield of the polymers of different runs are calculated as following: Run 1 and Run 2 are based on the total weight of AN and BVE (radical polymerization only); Runs 3 and 4 are based on the total weight of AN, BVE and CHO (radical and cationic polymerization); Run 5 is based on the total weight of AN, BVE, CHO and PVAc-OH.

[b] Determined by NMR.

[c] The polymers were recovered by precipitation using hexane.

[d] Part B in Fig. 1.

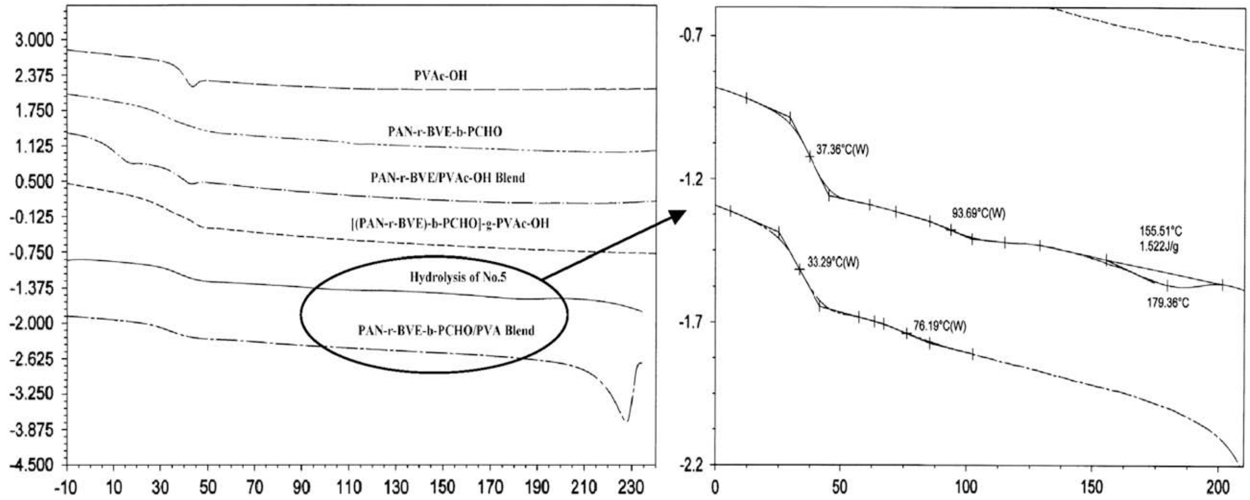

Fig. 2. DSC spectra for the polymers measured at a heating rate of 10 °C/min under a slow stream of nitrogen.

a helium–neon laser (632.8 nm, 22 mW). The scattering angle was fixed at 90°. Atomic force microscopy (AFM) measurements were performed on an SPI3800N/SPA-400 (SII Co. Japan) operating in the direct force microscope (DFM) mode. Samples for AFM were prepared as follows: Graft polymers were dissolved in a mixed solvent of DMSO/THF (1/5, v/v) at a concentration of 0.2 mg/mL. A few drops of the solution were put on a substrate of mica and then the solvent was evaporated at room temperature.

3. Results and discussion

3.1. Synthesis of a graft polymer

Table 1 indicates the conditions and result of synthesis of a graft polymer, PVAc-*g*-[P(AN-*r*-VBE)-*b*-PCHO], by radical/cationic transformation polymerization and coupling reaction. This table also contains conditions and results of reference systems. Run 1 in Table 1 indicates that polymerization of a mixture of AN/BVE/CHO initiated by AIBN yielded a statistical copolymer of AN and BVE (P(AN-*r*-BVE)) with a comonomer unit ratio of AN:BVE = 1.3:1.0, indicating that CHO was not polymerized radically and did not practically disturb the radical copolymerization of AN and BVE. As can be seen in run 2, polymerization of a mixture of AN/BVE/CHO initiated by AIBN in the presence of PVAc-OH also yielded P(AN-*r*-BVE). Comparing the yields and the comonomer unit ratios for runs 1 and 2, it is concluded that PVAc-OH exhibited no or only a little effect on the radical copolymerization of AN and BVE. This observation indicates that any propagating radicals of P(AN-*r*-BVE) do not couple with PVAc-OH. Run 3 represents polymerization of a mixture of AN/BVE/CHO initiated by AIBN in the presence of Ph_2IPF_6, which is a typical example of radical/cationic transformation polymerization. This polymerization yielded a block copolymer of P(AN-*r*-BVE) and poly(CHO) (P(AN-*r*-BVE)-*b*-PCHO) with a comonomer ratio of AN:BVE:CHO = 1.2:1.0:1.4. Run 4 indicates that only a very low yield (3.0%) of polymer was obtained from a mixture of AN/BVE/CHO in the presence of Ph_2IPF_6. This observation confirms that AIBN, a radical initiator, is necessary for the formation of P(AN-*r*-BVE)-*b*-PCHO. As reported previously [31,32], carbon radicals carrying electron-donating groups undergo electron transfer to Ph_2IPF_6 to form the corresponding cations whereas carbon radicals carrying electron-withdrawing groups (e.g., the radical derived from AIBN and PAN propagating radical) do not. In run 3, electron transfer occurs from P(AN-*r*-BVE) propagating radicals bearing BVE unit at the terminal to Ph_2IPF_6 to form the corresponding polymeric cations which initiate cationic polymerization of CHO, resulting in the formation of P(AN-*r*-BVE)-*b*-PCHO. Run 5 indicates that radical/cationic transformation polymerization of AN/BVE/CHO in the presence of PVAc-OH yielded a polymer of a comonomer unit ratio of AN/BVE/CHO/VAc = 1.2:1.0:1.5:0.90. Since P(AN-*r*-BVE) propagating radical does not couple with PVAc-OH (run 2), it is likely [23] that the polymer formed by the coupling of P(AN-*r*-BVE)-*b*-PCHO polymeric cations with PVAc-OH, as can be seen in Scheme 1 (i.e., the formation of a graft polymer).[1] The graft efficiency for the graft polymer was estimated to be 85% by $W_1/(W_1 + W_2)$, where W_1 and W_2 are the weights of grafts and the PVAc backbone, respectively.

Table 2
Glass transition temperatures (T_g or T_{g1}, and T_{g2}) and melting points (T_m) of the polymers obtained.

Polymer	T_g or T_{g1}, °C	T_{g2}, °C	T_m, °C
P(AN-*r*-BVE)	10	–	–
PCHO	70	–	–
P(AN-*r*-BVE)-*b*-PCHO	34	–	–
PVAc-OH	39	–	–
PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO]	26	43	–
P(AN-*r*-BVE)-*b*-PCHO/PVAc-OH blend	36	–	–
PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO]	37	94	179
P(AN-*r*-BVE)-*b*-PCHO/PVA blend	34	76	228

3.2. Characterization of graft polymers before and after hydrolysis

The PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer was hydrolyzed with NaOH to obtain a poly(vinyl alcohol)-based amphiphilic graft polymer (PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO]). Both the graft polymers were fully characterized by ^1H NMR, IR, GPC and DSC. ^1H NMR, IR and GPC data are shown in Figs. 1s–3s in Supporting information, respectively.

Table 2 lists glass transition temperatures (T_g or T_{g1}, and T_{g2}) and melting points (T_m) for the polymers determined by DSC measurements. In the case of PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer, two glass transitions were observed at 26 and 43 °C (T_{g1} and T_{g2}, respectively). Comparing with the T_g values for P(AN-*r*-

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[1] Polymers obtained by radical/cation transformation polymerization usually contain homopolymers of cationic polymerizable monomers because of chain transfer after radical/cation transformation. In the case of the synthesis of the graft polymer, the graft polymer was purified by careful fractionation (see Section 2).

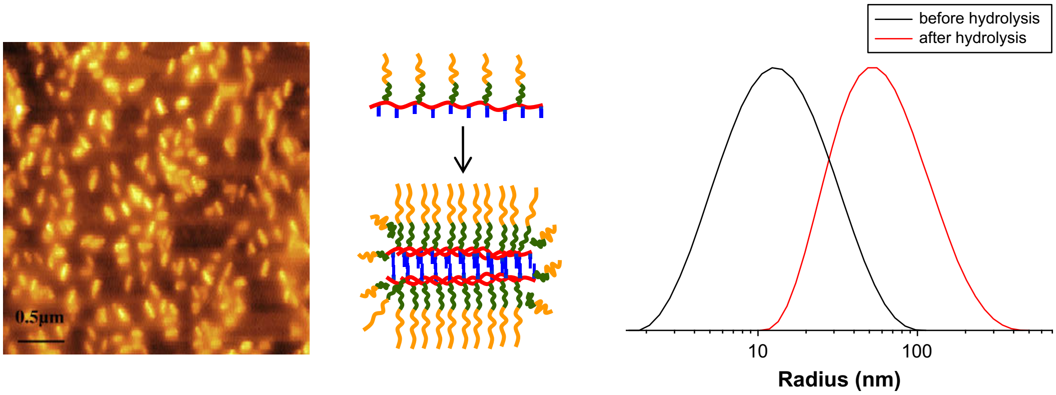

Fig. 3. AFM tapping topographic image and aggregation scheme of the hydrolyzed graft polymers of PVA-*g*-(PAN-*r*-PBVE-*b*-PCHO) and the DLS results of graft copolymers before and after hydrolysis.

BVE)-*b*-PCHO and PVAc-OH (34 and 39 °C, respectively), it is likely that T_{g1} and T_{g2} correspond to glass transitions for the P(AN-*r*-BVE)-*b*-PCHO grafts and the PVAc backbone, respectively. T_{g1} for PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer is slightly lower than T_g for P(AN-*r*-BVE)-*b*-PCHO presumably because propagation of PCHO was disturbed by the coupling reaction with PVAc-OH and the average molar mass of P(AN-*r*-BVE)-*b*-PCHO grafts was lower than that for P(AN-*r*-BVE)-*b*-PCHO obtained in the absence of PVAc-OH (run 1 in Table 1), whereas T_{g2} for PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer is slightly higher than T_g for PVAc-OH, indicating that the movement of the PVAc backbone is somehow restricted by the P(AN-*r*-BVE)-*b*-PCHO grafts. It should be noted here that the DSC result for PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer is different from that for blend of P(AN-*r*-BVE)-*b*-PCHO and PVAc-OH, in which both the polymers undergo glass transition at almost the same temperature (34 and 39 °C).

In the case of PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer, two glass transitions were observed at 37 and 94 °C (T_{g1} and T_{g2}, respectively). As temperature was further increased, melting was observed at 179 °C (T_m). Comparing with the T_{g1}, T_{g2} and T_m values for a blend of P(AN-*r*-BVE)-*b*-PCHO and PVA (36, 76 and 228 °C, respectively), it is likely that T_{g1} and T_{g2} correspond to glass transitions for the P(AN-*r*-BVE)-*b*-PCHO grafts and the PVA backbone, respectively, and that T_m corresponds to the melting of the PVA backbone. T_{g1} and T_{g2} for PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer are higher than those for the blend of P(AN-*r*-BVE)-*b*-PCHO and PVA, indicating that the movements of the P(AN-*r*-BVE)-*b*-PCHO grafts and the PVA backbone are restricted by each other. On the other hand, T_ms for PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer are lower than those for the blend of P(AN-*r*-BVE)-*b*-PCHO and PVA, indicating that the P(AN-*r*-BVE)-*b*-PCHO graft decreases T_m for the PVA backbone.

3.3. *AFM and DLS for the amphiphilic graft polymer*

Since the hydrolyzed graft polymer, PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO], is amphiphilic, aggregates formed from the polymer in a selective solvent were characterized by AFM and DLS. AFM of Fig. 3 (left) demonstrates an example of AFM images for the aggregates formed from PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer in a mixed solvent of DMSO/THF (1/5, v/v). This figure shows a number of ellipsoidal objects of 56 nm height, 160 nm length and 80 nm width. DLS of Fig. 3 (right) indicates hydrodynamic radius (R_H) distributions for hydrolyzed and non-hydrolyzed graft polymers, i.e., PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO] and PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO], measured in a mixed solvent of DMSO/THF (1/5, v/v). The average value of R_H for PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO] was determined to be 116 nm, which agreed well with the size of aggregates in the AFM image. On the other hand, the average value of R_H for PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO] graft polymer was also determined to be 26 nm, corresponding to molecularly dispersed polymer chains. The aggregation of PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO] in the DMSO/THF mixed solvent may be driven by strong hydrogen bonding interaction of hydroxyl groups on the PVA backbone.

4. Conclusions

In summary, a simple method for synthesis of graft polymers was developed. A graft polymer, PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO]) was synthesized successfully by "one-step" radical/cationic transformation polymerization of a mixture of AN/BVE/CHO and *in situ* coupling of P(AN-*r*-BVE)-*b*-PCHO grafts with PVAc-OH backbone. A PVA-based amphiphilic graft polymer, PVA-*g*-[P(AN-*r*-BVE)-*b*-PCHO]), was also synthesized by alkali hydrolysis of PVAc-*g*-[P(AN-*r*-BVE)-*b*-PCHO]). AFM and DLS measurements confirmed the formation of aggregates from the amphiphilic graft polymer. These results demonstrate that the radical/cationic transformation polymerization may supply a simple and promising approach to the synthesis of graft polymers.

Acknowledgments

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Appendix. Supporting information

^{1}H NMR, IR spectra, GPC, solubility data of the graft polymers. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.06.002.

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