Poly(vinyl pyrrolidone-*co*-vinyl acetate)-*graft*-poly(ε-caprolactone) as a Compatibilizer for Cellulose Acetate/Poly(ε-caprolactone) Blends

Tomokazu Higeshiro, Yoshikuni Teramoto, Yoshiyuki Nishio

Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan

Received 27 December 2008; accepted 2 March 2009
DOI 10.1002/app.30366
Published online 1 May 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(vinyl pyrrolidone-*co*-vinyl acetate)-*graft*-poly(ε-caprolactone) (PVPVAc-*g*-PCL) was synthesized by radical copolymerization of *N*-vinyl-2-pyrrolidone (VP)/vinyl acetate (VAc) comonomer and PCL macromonomer containing a reactive 2-hydroxyethyl methacrylate terminal. The graft copolymer was designed in order to improve the interfacial adhesiveness of an immiscible blend system composed of cellulose acetate/poly(ε-caprolactone) (CA/PCL). Adequate selections of preparation conditions led to successful acquisition of a series of graft copolymer samples with different values of molecular weight ($M_n^{\mathrm{PVPVAc-}g\mathrm{-PCL}}$), number of grafts ($n$), and segmental molecular weight of PVPVAc between adjacent grafts (M_n (between grafts)). Differential scanning calorimetry measurements gave a still immiscible indication for all of the ternary blends of CA/PCL/PVPVAc-*g*-PCL (72 : 18 : 10 in weight) that were prepared by using any of the copolymer samples as a compatibilizer. However, the incorporation enabled the CA/PCL (4 : 1) blend to be easily melt-molded to give a visually homogeneous film sheet. This compatibilizing effect was found to be drastically enhanced when PVPVAc-*g*-PCLs of higher $M_n^{\mathrm{PVPVAc-}g\mathrm{-PCL}}$ and M_n (between grafts) and lower n were employed. Scanning electron microscopy revealed that a uniform dispersion of the respective ingredients in the ternary blends was attainable with an assurance of the mixing scale of several hundreds of nanometers. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2945–2954, 2009

Key words: cellulose acetate; poly(ε-caprolactone); poly(vinyl pyrrolidone-*co*-vinyl acetate)-*graft*-poly(ε-caprolactone); macro monomer; compatibilizer; biodegradable; compatibilization; graft copolymers

INTRODUCTION

Naturally occurring polysaccharides represented by cellulose are sustainable resources and environmentally conformable substances. Now it is recognized that they possess a great deal of potential to be developed for new industrial applications in themselves or in combination with supplementary ingredients.[1] However, in general, there is an intractability of natural polysaccharides showing no thermal moldability and poor solubility in most organic solvents. Chemical modification of cellulosics makes it easier for processing, but attention should be paid to the respect that their original biodegradability is lost in some cases. A remedy for overcoming such problems could be improvement of thermal moldability of cellulosics by grafting[1–5] or blending[1,6–12] with biodegradable aliphatic polyeters.

Formerly, the authors provided an insight into the relationship between the ability of cellulose alkyl esters to form a miscible blend with poly(ε-caprolactone) (PCL) and the ester derivative structure in terms of the side-chain length (carbon number n, 2–7).[8,9] It was revealed that cellulose butyrate of $n = 4$ and cellulose valerate of $n = 5$ exhibit the highest miscibility on blending with PCL. However, biodegradable[13,14] and commodity-type cellulose acetate (CA) of $n = 2$ was judged to be immiscible with PCL over the entire composition range, although a certain material modification using the CA-PCL combination could be achieved by graft copolymerization.[2,4,5]

Immiscible polymer blends often show bad mechanical properties, particularly those associated with ductility, which preclude their utilization. A significant part of this problem comes from poor force transfer between the component phases in the blend material. It is believed that lower attractive forces between the phases lead to a premature failure of the material under stress as a result of the crack opening mechanisms.[15] Therefore, some methods to improve the phase adhesion and reduce the interfacial energy between the immiscible phases have been a subject of considerable research activity.[15–22] This process of stabilizing polymer blends is commonly called compatibilization.

Against the background mentioned above, an investigation was undertaken to newly design an effective compatibilizer that can enhance the

Correspondence to: Y. Nishio (ynishio@kais.kyoto-u.ac.jp).

adhesion stress generated between the separate phases in the immiscible CA/PCL blends. The designed copolymer is of a graft copolymer type, the trunk and graft segments being miscible or identical with one of the polymer components of the binary blends. For closing the incompatibility gap between the CA and PCL pair, *N*-vinyl-2-pyrrolidone (VP)-containing vinyl polymers miscible with CA[23–27] can be used as the trunk, and thus PCL itself is properly selected as the other ingredient of the graft copolymer. How can it be prepared? A potential route is graft copolymerization via a free radical mechanism with a "macromonomer" and comonomer.

There have been several examples dealing with the preparation of the kind of graft copolymers by means of the macromonomer precursor method;[17–19,28–30] the length and number (or density) of grafts in the copolymer product can be dictated, respectively, by the molecular weight of the macromonomer and by the in-feed ratio and mutual reactivity of the macromonomer/comonomer. In general, graft copolymers of lower graft density are known to act as an effective blend compatibilizer. Indeed, it was reported that one or two grafts per the trunk chain gave rise to an optimized enhancement in mechanical property of some compatibilized polymer blends,[19] which suggests that a di- or triblocklike structure is a preferred molecular architecture of blend compatibilizers. Higher molecular weights of both the trunk and graft chains would also be desirable.

In the present article, the synthesis of a graft copolymer composed of VP-containing vinyl polymer (trunk) and PCL (graft) and the estimation of its suitability as a compatibilizer for the immiscible CA/PCL pair are described. The synthesis was carried in two steps. First, 2-hydroxyethyl methacrylate (HEMA)-terminated PCL was prepared by ring opening polymerization of ε-caprolactone (CL) initiated at the hydroxyl group of HEMA. Then the HEMA-terminated PCL macromonomer was copolymerized with VP/vinyl acetate (VAc) comonomer. The VAc component was used in order to increase the flexibility of the trunk chain, as plain poly(vinyl pyrrolidone) (PVP) is generally brittle. Poly(vinyl pyrrolidone-*co*-vinyl acetate) (PVPVAc) is already ensured to be miscible with CA of the degree of acetyl substitution (DS) <2.8 unless the VP fraction in the vinyl copolymer is less than 25 mol %.[23,24] The synthesized graft copolymer, poly(vinyl pyrrolidone-*co*-vinyl acetate)-*graft*-poly(ε-caprolactone) (PVPVAc-*g*-PCL), was incorporated with a CA/PCL mixture and the compatibilizing effect was examined through measurements of tensile strength and blend morphology.

EXPERIMENTAL

Original materials

CA was kindly supplied by Daicel Chemical Industries. The DS and average degree of polymerization (DP) were 2.45 and 160, respectively; these values were determined by ^{1}H-NMR and GPC measurements, respectively. CL monomer was supplied as PLACCEL M by Daicel Chemical Industries and used after distillation. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Tokyo Chemical Industry. HEMA (Wako Pure Chemical Industries, Osaka, Japan), VP (Nacalai Tesuque, Kyoto, Japan), and VAc (Nacalai Tesuque) were distilled before use. Other solvents and chemicals were all guaranteed reagent-grade and used as received.

Preparation of HEMA-PCL macromonomer

0.15–0.73 g (1.15–5.61 mmol) of HEMA and 10–25 g (87.6–219 mmol) of CL were added into a flask. Subsequently, the flask was heated in an oil bath at 140°C with stirring under a dried nitrogen atmosphere. After 10 min, 84–168 μL (0.259–0.519 mmol) of tin (II) 2-ethylhexanoate was added into the flask and ring opening polymerization was conducted at the temperature for 1 h. After the polymerization, the flask was cooled in an ice bath and acetone was poured into the flask. The resulting homogeneous solution was added dropwise into a vigorously stirred, large excess of methanol. Each HEMA-PCL macromonomer obtained as the precipitate was filtered, washed with methanol several times, and dried at 40°C *in vacuo* for 24 h.

Preparation of PVPVAc-*g*-PCL

1.25–3.03 g (1.17–10.3 mmol for HEMA moiety) of HEMA-PCL and 10–80 mL of 1,4-dioxane were added into a flask. The mixture was stirred under a dried nitrogen atmosphere at 20°C. After the system became a transparent liquid, VP and VAc monomers (1 : 1 mol/mol) were added into the flask. The in-feed molar ratio of comonomer/HEMA-PCL macromonomer ranged from 500 to 1000. Subsequently, AIBN (0.01–0.02 mol % relative to the in-fed VP/VAc comonomer) was added into the flask, and the system was heated in an oil bath at 60°C. After 24 h, the flask was cooled in an ice bath. When the polymerization system was highly viscous or turbid, 50 mL of dichloromethane as diluent was added to give a homogeneous solution. The resultant solution was added dropwise into a vigorously stirred, large excess amount of diethyl ether. Each crude product obtained as the precipitate was filtered and then dried at 40°C *in vacuo*.

Further purification was performed in the following two-step process. Namely, PVPVAc uncombined with HEMA-PCL macromonomer was removed by extraction with distilled water for 48 h at room temperature. The water-insoluble fraction was dissolved in dichloromethane, and the solution was precipitated into diethyl ether. After drying at 40°C *in vacuo*, the water-insoluble part was extracted with a methanol/toluene mixture (80 : 20 in volume) and the HEMA-PCL component unreacted with VP/VAc comonomer and a possibly coexistent PCL homopolymer without HEMA terminal (see below) were removed as the insoluble residue by centrifugation. The soluble part in the methanol/toluene mixture was precipitated into an excess amount of diethyl ether. The ultimately remaining product, i.e. purified PVPVAc-*g*-PCL was filtered and dried at 40°C *in vacuo*.

Preparation of blends

CA/PCL/compatibilizer blends were prepared in film form from mixed polymer solutions. An aprotic polar *N*,*N*-dimethylformamide was selected as a common solvent. Solutions (1.0 wt %) of CA, PCL, and the compatibilizer were prepared separately and mixed with each other in the desired proportions. After stirring over a period of 24 h at 40°C, each mixed solution (transparent) was poured into a Teflon tray and a film sheet was made by solvent evaporation at 50°C under reduced pressure (<10 mmHg). The as-cast samples were further dried at 40°C *in vacuo* for 3 days.

For supply particularly to tensile measurements and SEM observations, the solution-cast blends were molded into a film sheet 0.1 mm thick by using a Toyo-Seiki hot-pressing apparatus. For the molding at 190°C, pressure was applied to the respective molten sample gradually to reach 5 MPa in 2.5 min; subsequently, it was increased quickly to 15 MPa, and this application was maintained for 30 s. Following this, as soon as the pressure was released, the sample was transferred to another compressing apparatus and quickly cold-pressed at 25°C and 15 MPa for 2 min. After being released again from the compressed state, the molded polymer sheet was finally conditioned at 20°C and 60%RH for 48 h.

Measurements

The molecular weights of HEMA-PCL and PVPVAc-*g*-PCL were determined by using a JASCO GPC-900 apparatus equipped with a refractive index detector. *N*,*N*-dimethylforamide (DMF) containing 10 m*M* LiBr was used as the mobile phase at a flow rate of 0.5 mL/min. The concentration and injection quantity of the test sample were 0.11 wt % and 50 μL, respectively. The system was calibrated with monodisperse polystyrene standards.

^{1}H-NMR spectra (300 MHz) were measured at 18°C on a Varian INOVA300 NMR apparatus. The solvent was $CDCl_3$ and the solute concentration was 16 mg/mL. Tetramethylsilane was employed as an internal standard. A pulse width of 3 μs was used and 32 scans were conducted.

Differential scanning calorimetry (DSC) was carried out with a Seiko DSC6200/EXSTAR6000 apparatus. The temperature proof-readings were calibrated with an indium standard. The calorimetry measurements were made on ca. 5-mg samples at a scanning rate of 20°C/min under a nitrogen atmosphere. The samples were first heated to 260°C and immediately quenched to −140°C. In this first cycle, the thermal histories of the respective samples were equalized completely. Then the second scans were run from −140°C to 260°C to record stable thermograms. The glass transition temperature (T_g) was determined from the midpoint of the discontinuity in heat flow.

Apparent flow temperatures of blend samples were measured by a constant heating test with a Shimadzu CFT-500A flow tester under a pressure of 50 MPa. The starting temperature was 50°C and the heating rate was 5°C/min. The die orifice size was 1 mm diameter and 10 mm length.

Tensile behavior was examined for hot-pressed film sheets at 20°C and 60% RH by using a Shimadzu Autograph AGS-1kNG. Specimens of rectangular shape ($20 \times 5 \times 0.1$ mm^3) were cut from the respective sheets. The strain rate and span length were 5 mm/min and 20 mm, respectively. Ten specimens of each blend sample were employed for the measurement and the averaged data were adopted.

Morphological observations of the fracture cross-sections of as-cast films and hot-pressed sheets were made by using a JEOL JSM-T330A SEM apparatus operated at 10 kV. The samples were coated with Au by spattering.

RESULTS AND DISCUSSION

Synthesis of compatibilizer

In order to obtain a compatibilizer for the immiscible CA/PCL pair, we executed the synthesis of PCL macromonomers bearing an acrylic function (i.e. HEMA) at one of their ends, and their free radical copolymerization with VP/VAc comonomer. For preparation of this kind of macromonomers, the use of a tin (II) 2-ethylhexanoate (Sn(II)Eht) catalyst is convenient because the ring opening polymerization of cyclic esters such as lactides and CL can be initiated efficiently by hydroxyl groups in the presence of Sn(II)Eht.[1,31–35] In the present study, more than

TABLE I
Preparation Conditions and Characterization of HEMA-PCL Macromonomers Obtained by Ring Opening Polymerization of CL in the Presence of Sn(II)Eht at 140°C for 1 h

Sample code	In-feed/mmol			Terminal HEMA content (%)	Molecular weight	
	HEMA	CL	Sn(II)Eht		$M_n^{\mathrm{HEMA-PCL}}$ (10^3)	Polydispersity
HEMA-PCL5.9k	5.60	91.0	0.26	84.0	5.9	1.55
HEMA-PCL13.4k	2.15	180.0	0.52	68.0	13.4	1.90
HEMA-PCL19.0k	1.39	225.0	0.52	65.6	19.0	1.97
HEMA-PCL29.5k	1.15	228.5	0.52	80.0	29.5	2.08

95% of in-feed CL monomer was recovered as the polymerized product after purification. The result of the HEMA-PCL synthesis is summarized in Table I. Four products were obtained and their number-average molecular weight was determined to be in the range 5.9–29.5 $\times$ 10^3 by GPC. Figure 1 demonstrates an ^{1}H-NMR spectrum of one of the products. In analogy with the previous study on the HEMA-functionalized poly(L-lactide),[29] the incorporation of HEMA moiety can be confirmed by this spectrum. In Figure 1, the resonance signals of the methacrylic double-bond hydrogens are observed at 6.14 and 5.60 ppm. In addition, one sharp multiplet centered at 4.34 ppm can be distinguished, and it is assigned to the four hydrogens of the oxyethylene residue of HEMA moiety. The methyl protons of the HEMA moiety give a sharp triplet at 1.95 ppm. When we denote the resonance peak areas of the unsaturated protons of HEMA terminal and that of the $C_{\varepsilon'}$ methylene protons of PCL terminal by **a** and **a**′, and ε′, respectively, a terminal HEMA content (in mol %) in the product can be determined by

$$\text{Terminal HEMA content } (\%) = 100(\mathbf{a} + \mathbf{a}')/\varepsilon' \quad (1)$$

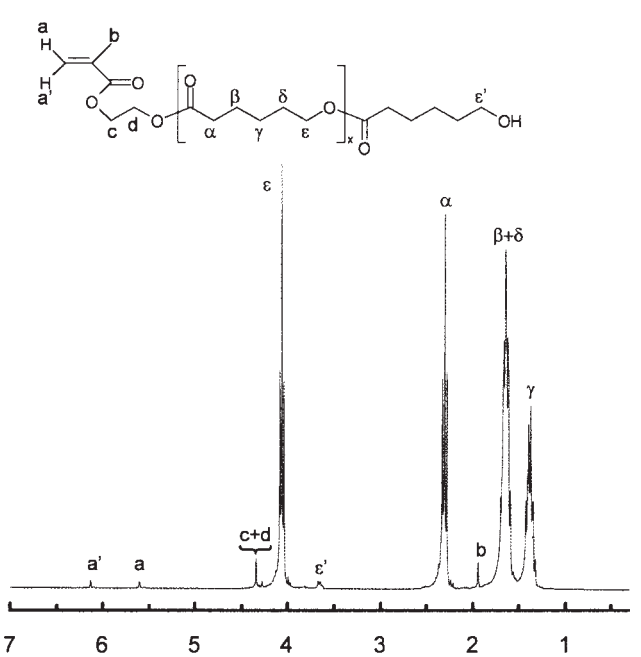

Figure 1 ^{1}H-NMR spectrum of HEMA-PCL5.9k.

As listed in Table I, the terminal HEMA contents of the four products were determined to be 65.6–84.0 %, respectively. From the conversion data, PCL chains without HEMA moiety are considered to have been produced by the polymerization initiated by a trace amount of water in the reaction system. Assuming that there is no difference in the molecular weight distribution between the PCLs with or without HEMA moiety, we regard the number-average molecular weights (5.9–29.5 $\times$ 10^3) determined by GPC as the ones of HEMA-PCL ($M_n^{\mathrm{HEMA-PCL}}$). A code HEMA-PCL*x*k in the table represents the macromonomer whose $M_n^{\mathrm{HEMA-PCL}}$ is $x \times 10^3$. The PCL homopolymer without HEMA terminal is able to be virtually removed in the purification of the following radical polymerization products.

The free radical copolymerization of VP/VAc comonomer with different HEMA-PCL macromonomers was carried out at 60°C in 1,4-dioxane. In all the reactions, the products were first separated into water-soluble and -insoluble fractions, where PVPVAc uncombined with HEMA-PCL could be removed as the soluble part (first purification). Subsequently, the water-insoluble fraction was extracted with methanol/toluene mixture (80 : 20 in volume), whereby both unreacted PCL macromonomer and PCL initially without HEMA terminal were removed as the second insoluble part (second purification). After centrifugation, the soluble part was reprecipitated in diethyl ether. Eventually, the objective graft copolymer, PVPVAc-*g*-PCL, was obtained after drying. The final yield of PVPVAc-*g*-PCL was 25–35 wt % relative to the total amount of in-feed VP/VAc comonomer and HEMA-PCL macromonomer.

Table II lists the radical copolymerization conditions and the result of the characterization of the graft products. Figure 2 exemplifies GPC chromatograms of HEMA-PCL29.5k and its copolymerized product #6 obtained after the first and second purification. It was found that the two-step purification

TABLE II
Radical Copolymerization of VP/VAc Comonomer with HEMA-PCL in 1,4-Dioxane at 60°C for 24 h, and Characterization of PVPVAc-*g*-PCL

Sample code	$M_n^{\text{HEMA-PCL}}/10^3$	In-feed (mol/L-dioxane) VP	VAc	HEMA-PCL	Molecular weight $M_n^{\text{PVPVAc-}g\text{-PCL}}/10^3$	poly-dispersity	Introduced VP/VAc molar ratio	w_{PCL}	n	M_n (between grafts)(10^3)
#1	5.9	1.30	1.30	5.12×10^{-3}	57.9	4.80	0.73/0.27	0.53	5.20	4.39
#2	13.4	5.05	5.05	4.67×10^{-3}	116	6.71	0.72/0.28	0.31	2.68	21.7
#3	13.4	1.25	1.25	1.17×10^{-3}	43.8	3.05	0.71/0.29	0.53	1.73	7.53
#4	19.0	5.05	5.05	4.76×10^{-3}	95.2	5.47	0.64/0.36	0.47	2.35	15.0
#5	19.0	2.55	2.55	3.30×10^{-3}	46.1	4.05	0.56/0.44	0.42	1.02	13.2
#6	29.5	5.10	5.10	5.13×10^{-3}	127	5.39	0.60/0.40	0.46	1.98	23.0
#7	29.5	1.70	1.70	1.70×10^{-3}	67.0	3.14	0.69/0.31	0.42	0.95	19.9
#8	29.5	10.5	10.5	1.03×10^{-2}	125	6.74	0.58/0.42	0.46	1.95	22.9

procedure successfully removed PVPVAc and unreacted HEMA-PCL macromonomer, because no corresponding peak was observed in the low molecular weight region of the ultimate GPC curve for #6. Thus, the series of purification was proven to be an effective separation technique for isolating PVPVAc-*g*-PCL from a reaction mixture of the free radical copolymerization of VP/VAc and HEMA-PCL macromonomer. As a result of the fractionation, the conversion of the in-fed VP/VAc monomers into the desired PVPVAc-*g*-PCL was determined to be 15–20%, while the rest VP/VAc formed ungrafted PVPVAc. Such a low incorporation of VP/VAc may be attributed to the inherent low reactivity of these monomers with HEMA-PCL. The number average molecular weight of the graft copolymers ($M_n^{\text{PVPVAc-g-PCL}}$) and the polydispersity (M_w/M_n) are listed in Table II.

Figure 3 illustrates an ^{1}H-NMR spectrum of a graft copolymer (#2 in Table II). The VP/VAc/HEMA-PCL composition was determined by resonance-peak analysis. When we designate the resonance peak areas of the C_B methyne of VAc, the C_F methylene of VP, and the C_ε methylene of PCL by **B**, **F**, and ε, respectively, the introduced VP/VAc molar ratio and PCL weight fraction (w_{PCL}) in the graft copolymer can be determined by eqs. (2) and (3), respectively.

$$\text{Introduced VP/VAc molar ratio} = \text{F}/2\text{B} \quad (2)$$

$$w_{\text{PCL}} = (\varepsilon \times 114.14)/(\mathbf{B} \times 2 \times 86.09 + \mathbf{F} \times 111.14 + \varepsilon \times 114.14) \quad (3)$$

where 114.14 is a molecular weight of oxycaproyl unit, and 111.14 and 86.09 are the ones of VP and VAc units, respectively. In the calculation of w_{PCL}, a contribution of the HEMA moiety as a joint of the PCL chains was neglected; in fact, the relative

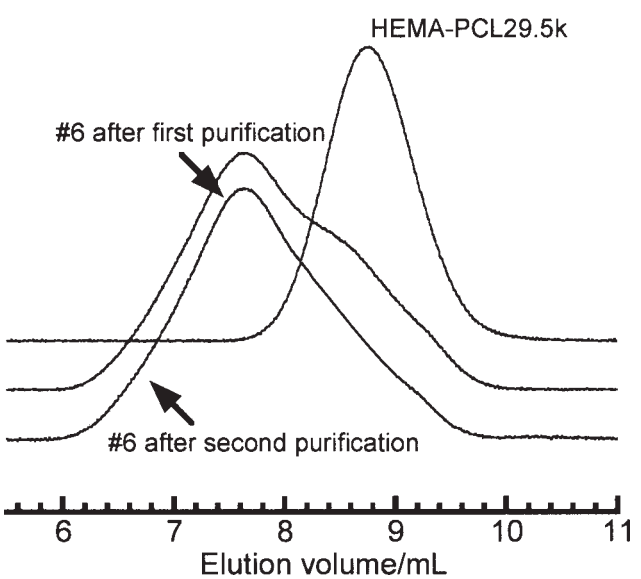

Figure 2 GPC chromatograms of HEMA-PCL29.5k, and of PVPVAc-*g*-PCL#6 after the first and second purifications.

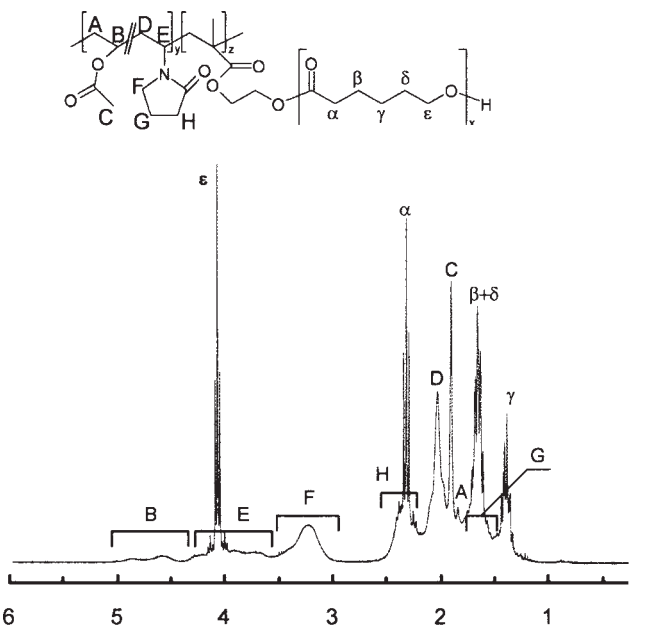

Figure 3 ^{1}H-NMR spectrum of PVPVAc-*g*-PCL#2.

HEMA content in the respective graft copolymers was too small to be evaluated directly by the NMR measurement. Then, the average number of grafts per trunk chain (n) was estimated by

$$n = M_n^{\mathrm{PVPVAc-g-PCL}} \times w_{\mathrm{PCL}} / M_n^{\mathrm{HEMA-PCL}} \quad (4)$$

The number average molecular weight between grafts (M_n(between grafts)) is determined by

$$M_n\,(\mathrm{between\,grafts}) = (M_n^{\mathrm{PVPVAc-g-PCL}} - M_n^{\mathrm{HEMA-PCL}} \times n) / (n+1) \quad (5)$$

These composition parameters of the graft copolymers are tabulated in Table II. The data shows a trend that, as $M_n^{\mathrm{HEMA-PCL}}$ increases, the number of grafts n decreases even though the in-feed amounts of HEMA-PCL are mutually at the same level (compare between #1, 2, 4, and 6). This result indicates a lower reactivity of the unsaturated acrylic group in the more voluminous macromonomers. Here, it should be recalled that this kind of copolymers with a lower graft density can be more effective blend compatibilizers. Taking into consideration the generally low reactivity of HEMA-PCL with VP/VAc comonomer, the radical polymerization was conducted with a high comonomer/HEMA-PCL molar ratio (760–1000 for #2–8) to prevent the increase in n and the decrease in M_n (between grafts). In consequence, $M_n^{\mathrm{PVPVAc-g-PCL}}$ and M_n (between grafts) assumed fairly large values as well as n decreased, according to expectation; however, the polydispersity in molecular weight of the respective graft copolymers was relatively high. The high polydispersity may be attributed to a possible chain-transfer reaction of VP monomer due to its particularly low copolymerization reactivity, as a similar transferring habit of VP has been reported before.[29,30] In a control experiment, such a high polydispersity (4.5–7.0) was observed even for plain PVP when VP was polymerized under the same conditions as the above.

Thermal analysis of compatibilizer

The graft copolymers were analyzed by DSC. Figure 4 displays thermograms of the graft copolymers in the second heating scan. Glass transition temperature T_g was evaluated as the midpoint of a baseline shift appearing in the respective DSC thermograms. For PVPVAc-g-PCL #4, 6 and 8, two T_gs were clearly observed on an enlarged scale of the thermograms. The higher T_g at 119–133°C is due to the backbone segments rich in VP/VAc and the lower one at −63 to −48°C is due to the PCL segments in the side chains. Thus, the vinyl copolymer and polyester constituents are obviously phase-separated. T_g of PCL segments was unclear for #2, reflecting the lowest w_{PCL} (0.31), whereas T_g of the backbone segments was usually detectable for high $M_n^{\mathrm{PVPVAc-g-PCL}}$-samples (#2, 4, 6, and 8). On the other hand, a crystalline structure of PCL was developed in all the graft copolymers except #1 that has a much shorter PCL graft-chain ($M_n^{\mathrm{HEMA-PCL}} = 5.9 \times 10^3$). Concerning those crystallizable samples, a considerable number of PCL segments were involved in the crystallization in the cooling scan. As to #2–5, however, an exothermic signal of cold-crystallization was also observed in the second heating scan, reflecting a relatively slow kinetics of melt-crystallization of these samples due to the moderate value of $M_n^{\mathrm{HEMA-PCL}}$ (13.4 or 19.0 × 10^3).

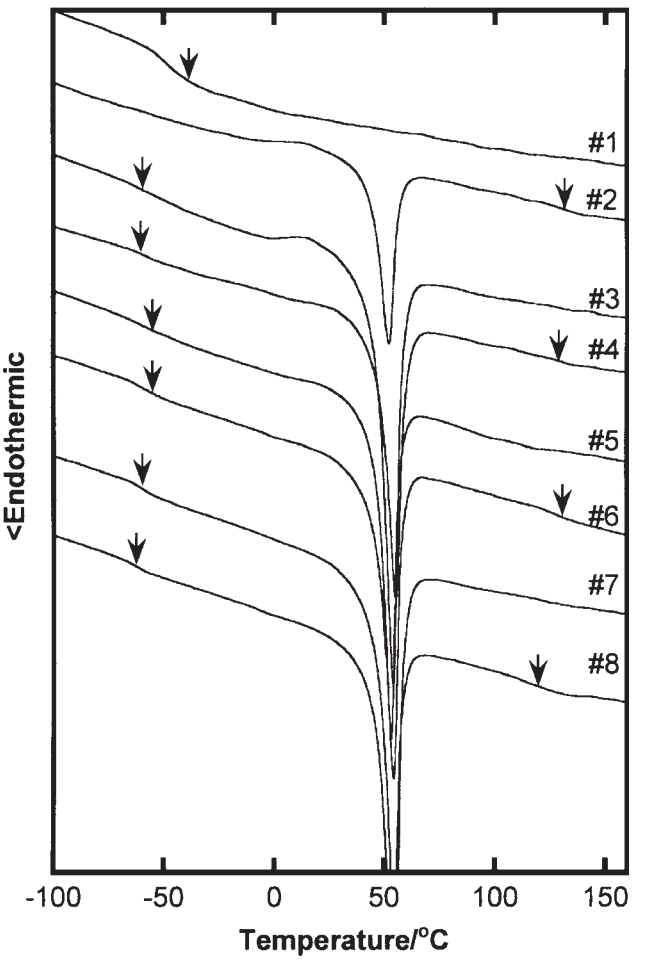

Figure 4 DSC thermograms (second heating) of PVPVAc-g-PCL#1–8. Arrows indicate the T_g positions.

Ternary blends

Ternary blends of CA, PCL, and PVPVAc-g-PCL were prepared by dissolution in DMF and casting. Traditional plasticization of CA has been accomplished by using as much as 30 wt % of low-molecular-weight plasticizers, such as phthalates, glycerol

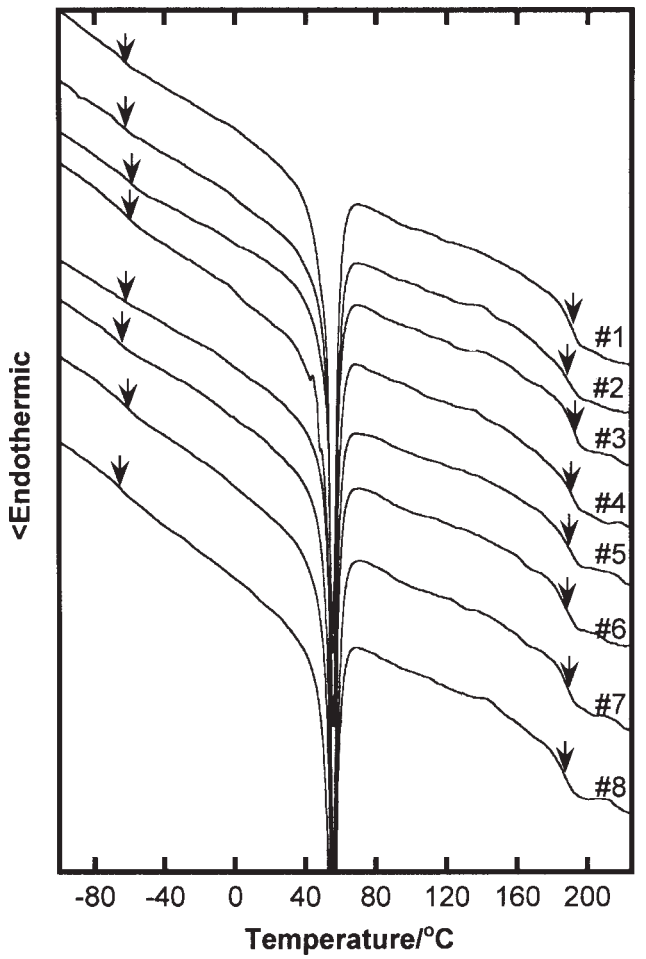

Figure 5 DSC thermograms (second heating) of ternary blends of CA/PCL/PVPVAc-*g*-PCL (72 : 18 : 10 in weight). Arrows indicate the T_g positions. The codes #1–8 denote the graft copolymers used as compatibilizers (see Table II).

derivatives, phosphates, etc. In view of the conditions, we fixed CA : PCL = 4 : 1 (in weight) and 10-wt % addition of compatibilizer for the ternary blend composition in the present study. Namely, the weight ratio of CA, PCL, and PVPVAc-*g*-PCL was set at 72 : 18 : 10. By this addition of the graft copolymer compatibilizer, the visual homogeneity of the ternary blends was generally improved in comparison with that of the corresponding CA/PCL blend (80 : 20 in weight) without compatibilizer. Particularly, in the case of adding #2, 4, 6, and 8 of PVPVAc-*g*-PCL, the as-cast films of the ternary blends were highly transparent. When the graft copolymers #1, 3, 5, and 7 were used as compatibilizers, however, the improvement in optical homogeneity was of a lesser extent. These observations suggest that a key to enhancing the homogeneity of the blend films is a higher value of $M_n^{\text{PVPVAc-g-PCL}}$, roughly $>100 \times 10^3$.

The ternary blends were also analyzed by DSC. Figure 5 shows their thermograms obtained in the second heating scan. For all the samples, two distinct T_gs were observed at around −60°C (PCL) and 190°C (CA), indicating that the CA and PCL components are essentially phase-separated even though the compatibilizer is added into the blend system. Thus, the scale of polymer-polymer mixing in any of the blends is larger than the T_g-detection scale that is usually assumed to be less than a couple of tens of nanometers.[36–38]

To prepare a series of samples for tensile measurements, thermal molding was performed for the solution-cast blends at 190°C. This molding temperature was determined as an apparent flow temperature (around 190°C) in flow testing for the ternary blends. Film sheets of CA/PCL (20–30 wt % PCL) molded without compatibilizer were quite brittle and hardly endurable to follow the tensile behavior. Ternary blend sheets could be made by thermal molding; however, as to the blends with #1, 3, 5, and 7 of PVPVAc-*g*-PCL, specimens for the tensile test could not be cut out from the respective molded sheets, which were still brittle. In contrast, with #2, 4, 6, and 8, test specimens were successfully obtained from the ternary blend sheets. The higher performance level of these graft copolymers as compatibilizer may be directly related to the higher $M_n^{\text{PVPVAc-g-PCL}}$, again.

Tensile mechanical properties were evaluated from stress–strain curves for the four ternary blend sheets with #2, 4, 6, and 8. The data of tensile strength, elongation at break, and Young's modulus are listed in Table III. Compared with the gross brittleness of the binary CA/PCL sheets, the properties of the ternary blend sheets were undoubtedly enhanced, more or less. An appropriate localization of the respective graft copolymers in the interfacial region between the two phase-separated polymer domains would account for the enhancement. In a careful assessment, the ternary blend with #4 showed somewhat higher strength and ductility compared with the blend with #2. The result suggests that PVPVAc-*g*-PCL can interact with the PCL phase of the blend concerned, more strongly, as the side-chain length and therefore $M_n^{\text{HEMA-PCL}}$ is

TABLE III
Mechanical Properties of CA/PCL/PVPVAc-*g*-PCL Blends (72 : 18 : 10 in weight)

Sample code	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
#2	23	4.2	1.29
#4	28	4.7	1.59
#6	35	6.2	1.06
#8	16	4.4	0.98

Measured at 20°C.

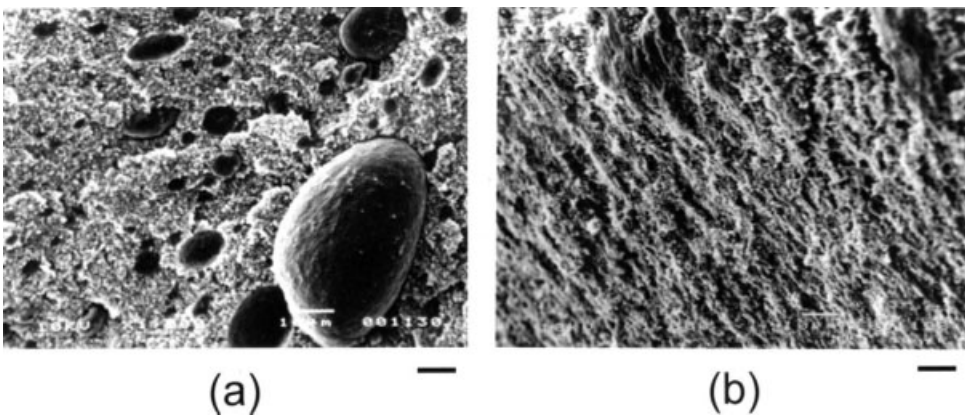

Figure 6 SEM images of the fracture cross-section of as-cast films of (a) CA/PCL (80 : 20 in weight) and (b) CA/PCL/PVPVAc-*g*-PCL#6 (72 : 18 : 10 in weight). Scale bars denote 10 μm.

increased. The blend with #6 exhibited better properties in strength and elongation at break than any other blends, presumably owing to the higher values of both $M_n^{\mathrm{PVPVAc-g-PCL}}$ and $M_n^{\mathrm{HEMA-PCL}}$ of the compatibilizer. These observations are interpretable in terms of a simple adhesion theory; viz., the longer chain-length of both the trunk and graft of PVPVAc-*g*-PCL could be favorable for their deep penetrations into the CA and PCL phases, respectively, and for their entanglements with the corresponding compatible partner as well. Here it should be noted that the ternary blend with #8 showed comparatively low tensile strength, although the graft copolymer has higher $M_n^{\mathrm{PVPVAc-g-PCL}}$ and $M_n^{\mathrm{HEMA-PCL}}$ equal to those of #6. This might have arisen from the higher polydispersity in molecular weight of the graft copolymer (see Table II). There appears a similar difference in the polydispersity between the copolymers #2 and 4, which may also be partly responsible for the superiority of #4 to #2 in the performance as compatibilizer.

Blend films cast from DMF solution were subjected to SEM observations. Figure 6(a) shows a surface morphology for the fracture cross-section of an unmodified blend (CA/PCL = 80/20), demonstrating the "ball and socket" formations due to segregation into the CA and PCL phases. It can be assumed that the dispersed globules are the PCL particles, taking account of the weight composition of the blend. The size of the individual PCL particles was estimated to be 10–30 μm. Upon blending CA and PCL with the compatibilizer PVPVAc-*g*-PCL#6 (72 : 18 : 10 in weight), a drastic change in the morphology occurred, as exemplified in Figure 6(b). The fracture cross-section of the ternary blend film shown there bears evidence of numerous fine entities having been pulled out instead of the "ball and socket" formations, and there are no longer the distinctly visible polymer domains of >1 μm. Therefore, the respective components are judged to be mixed in a scale of less than several hundreds of nanometers. It can also be assumed that the addition of the graft copolymer to the completely incompatible CA/PCL blend increased extraordinarily the interfacial adhesion between the phase-separated polymer domains.

Figure 7 compiles SEM images of the fracture sections of film sheets prepared by hot-pressing selected cast blends. These images were taken for the vicinity of the edge of the respective fracture surfaces, consequently involving the actually pressed surface of the films (designated as PS in micrographs). The relatively rough structure region in the respective images corresponds to the surface of the fracture section. As can be seen in Figure 7(a), the uncompatibilized blend of CA/PCL = 80/20 displayed a rather heterogeneous morphology not only on the fracture section but also on the pressed surface of the molded sheet. In contrast, in molded samples of the ternary blends containing compatibilizer #2, 6, and 8 [Fig. 7(b–d)], the pressed surface was quite smooth and the homogeneity of the fracture section was also better. In particular, a highly homogeneous fracture section was observed for the ternary blend with #6 [Fig. 7(c)]. This observation is in accordance with the finding of the most improved tensile properties for the blend sample. These complementary results evidence well that this compatibilizer reduces the interfacial energy and thereby produces a finer and more uniform morphology in the CA/PCL matrix. The higher $M_n^{\mathrm{PVPVAc-g-PCL}}$ and $M_n^{\mathrm{HEMA-PCL}}$ of #6 are likely to be contributory to the better performance as a compatibilizer.

CONCLUSION

We developed a new graft copolymer, PVPVAc-*g*-PCL, having quite a low number of grafts ($n < 3$) for improving the compatibility of CA with PCL. The

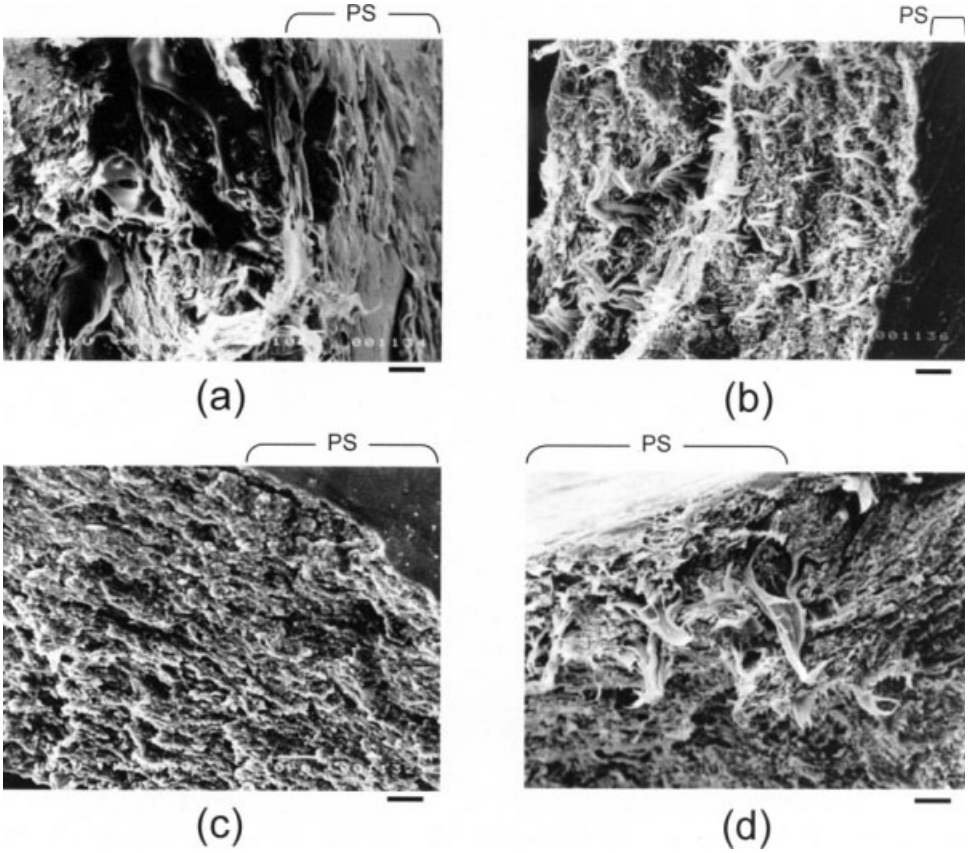

Figure 7 SEM images of the fracture cross-section of molded film sheets of (a) CA/PCL (80/20) blend without compatibilizer and (b–d) ternary blends of CA/PCL/PVPVAc-*g*-PCL (72/18/10). PVPVAc-*g*-PCL: (b) #2; (c) #6; (d) #8. PS designates the pressed surface of the respective film sheets. Scale bars denote 10 μm.

VP-containing vinyl polymer as a trunk chain is known to be miscible with CA. It was demonstrated that the combination of the ring opening polymerization of CL initiated at the hydroxyl groups of HEMA and the free radical copolymerization of VP, VAc, and HEMA-PCL macromonomer was a successful route in preparing the PVPVAc-*g*-PCL copolymers. Blends of CA and PCL are even optically and mechanically incompatible, showing large phase-separated polymer domains and poor interfacial adhesion between the two phases, and thus they are difficult to be processed in visually homogeneous film form. It was found that PVPVAc-*g*-PCL of higher molecular weights associated with both the trunk and graft chains is much more effective in enhancing the compatibility between CA and PCL. By the use of such an adequate graft copolymer as a compatibilizer, the thermal molding of CA/PCL blends became easier and the tensile mechanical properties were extraordinarily improved, especially in toughness as a sheet material. In a morphological support by SEM, a fine dispersion of the constituent polymer domains was attained in the well-compatibilized blends, with an assessment of the mixing scale of less than at least several hundreds of nanometers.

References

1. Nishio, Y. Adv Polym Sci 2006, 205, 97.
2. Teramoto, Y.; Ama, S.; Higeshiro, T.; Nishio, Y. Macromol Chem Phys 2004, 205, 1904.
3. Teramoto, Y.; Nishio, Y. Polymer 2003, 44, 2701.
4. Teramoto, Y.; Yoshioka, M.; Shiraishi, N.; Nishio, Y. J Appl Polym Sci 2002, 84, 2621.
5. Kusumi, R.; Teramoto, Y.; Nishio, Y. Macromol Chem Phys 2008, 209, 2135.
6. Buchanan, C. M.; Gedon, S. C.; Pearcy, B. G.; White, A. W.; Wood, M. D. Macromolecules 1993, 26, 5704.
7. Buchanan, C. M.; Gedon, S. C.; White, A. W.; Wood, M. D. Macromolecules 1992, 25, 7373.
8. Kusumi, R.; Inoue, Y.; Shirakawa, M.; Miyashita, Y.; Nishio, Y. Cellulose 2008, 15, 1.
9. Nishio, Y.; Matsuda, K.; Miyashita, Y.; Kimura, N.; Suzuki, H. Cellulose 1997, 4, 131.
10. Scandola, M. Can J Microbiol 1995, 41, (Suppl. 1) 310.
11. Scandola, M.; Ceccorulli, G.; Pizzoli, M. Macromolecules 1992, 25, 6441.
12. Schulze, K.; Kressler, J.; Kammer, H. W. Polymer 1993, 34, 3704.

13. Buchanan, C. M.; Gardner, R. M.; Komarek, R. J. J Appl Polym Sci 1993, 47, 1709.
14. Sakai, K.; Yamauchi, T.; Nakasu, F.; Ohe, T. Biosci Biotechnol Biochem 1996, 60, 1617.
15. Barlow, J. W.; Paul, D. R. Polym Eng Sci 1984, 24, 525.
16. Xanthos, M. Polym Eng Sci 1988, 28, 1392.
17. Barakat, I.; Dubois, P.; Jerome, R.; Teyssie, P.; Goethals, E. J Polym Sci Part A: Polym Chem 1994, 32, 2099.
18. Chung, T. C.; Rhubright, D. Macromolecules 1994, 27, 1313.
19. Peiffer, D. G.; Rabeony, M. J Appl Polym Sci 1994, 51, 1283.
20. Koning, C.; Van Duin, M.; Pagnoulle, C.; Jerome, R. Prog Polym Sci 1998, 23, 707.
21. Mani, R.; Tang, J.; Bhattacharya, M. Macromol Rapid Commun 1998, 19, 283.
22. Tamura, N.; Ban, K.; Takahashi, S.; Kasemura, T.; Obuchi, S. J Adhes 2006, 82, 355.
23. Miyashita, Y.; Suzuki, T.; Nishio, Y. Cellulose 2002, 9, 215.
24. Ohno, T.; Nishio, Y. Macromol Chem Phys 2007, 208, 622.
25. Ohno, T.; Nishio, Y. Macromolecules 2007, 40, 3468.
26. Ohno, T.; Nishio, Y. Cellulose 2006, 13, 245.
27. Ohno, T.; Yoshizawa, S.; Miyashita, Y.; Nishio, Y. Cellulose 2005, 12, 281.
28. Gnanou, Y.; Rempp, P. Makromol Chem 1987, 188, 2111.
29. Eguiburu, J. L.; Berridi, M. J. F.; Sanroman, J. Polymer 1995, 36, 173.
30. Eguiburu, J. L.; Fernandezberridi, M. J.; Roman, J. S. Polymer 1996, 37, 3615.
31. Kowalski, A.; Duda, A.; Penczek, S. Macromol Rapid Commun 1998, 19, 567.
32. Kricheldorf, H. R.; Kreisersaunders, I.; Boettcher, C. Polymer 1995, 36, 1253.
33. Kricheldorf, H. R.; Kreiser-Saunders, I.; Stricker, A. Macromolecules 2000, 33, 702.
34. Storey, R. F.; Taylor, A. E. J Macromol Sci: Pure Appl Chem 1998, 35, 723.
35. Veld, P.; Velner, E. M.; Vandewitte, P.; Hamhuis, J.; Dijkstra, P. J.; Feijen, J. J Polym Sci Part A: Polym Chem 1997, 35, 219.
36. Kaplan, D. S. J Appl Polym Sci 1976, 20, 2615.
37. Nishio, Y. Cellulosic Polymers, Blends and Composites, R.D., Gilbert, Ed. Hanser Pub.: New York, 1994; Chapter 5.
38. Ultracki, L. A. Polymer Alloys and Blends, Hanser Publishers: Munich, 1990.