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Solution copolymerization of D-lactose-*O*-(*p*-vinylbenzyl)-hydroxime with acrylonitrile

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Copolymerization of D-lactose-*O*-(*p*-vinylbenzyl)-hydroxime (LVH), a new vinyl monomer, with acrylonitrile (AN) was performed in DMSO with AIBN as the initiator. The conversion of LVH is much faster than that of AN and reaches 100% in 2 h. The reactivity ratios of LVH and AN, as determined by the extended Kelen–Tüdös method, are 1.0975 and 0.0554, respectively. Increasing the proportion of LVH in the monomer mixture significantly increases the LVH content in the copolymer. The conversion of monomers and the AN content in the copolymer rise gradually with increasing reaction time and initiator concentration. The number average molecular weights of the copolymers are independent of the monomer feed ratios. The LVH-*co*-AN copolymers exhibit lower glass transition temperatures than PLVH homopolymer. The presence of small amounts of LVH in the copolymer chain reduce the cyclization of nitrile groups in AN segments of the copolymer. Complete disappearance of nitrile cyclization is observed when the contents of LVH reaches and exceeds 16.9%. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: D-lactose-*O*-(*p*-vinylbenzyl)-hydroxime (LVH); lactose moiety; copolymer)

INTRODUCTION

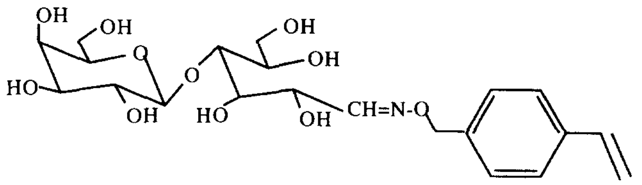
Converting lactose into polymerizable structures offers new opportunities for the utilization of lactose which is a major component of whey permeate, an under utilized by-product from the cheese industry. Incorporating the lactose moiety in polymer structures also creates unique chemical functionalities for novel polymers. In our recent work[1], a new vinyl monomer containing a lactose moiety as the side group, i.e., D-lactose-*O*-(*p*-vinylbenzyl)-hydroxime (LVH), was synthesized. This monomer can be polymerized in aqueous medium with a redox initiator. The homopolymer of LVH is water soluble and exhibits adhesive behavior. The hydrophilicity of the lactose moiety makes this LVH monomer a desirable candidate for copolymerization with other vinyl monomers to yield resins for new functional properties.

Acrylonitrile (AN) has a broad range of applications as fibers, both as textiles and as precursors to carbon fibers, membranes, and engineering plastics. For some applications, such as textiles and membranes, hydrophilicity and biocompatibility are desirable. Considerable attention has been given to the improvement in these characteristics of PAN[2–6]. Copolymerization of AN is among the methods for such structural improvement[7–10]. This paper reports the copolymerization of LVH with AN in DMSO using 2,2′-azobisisobutyronitrile as the initiator. The characteristics of the copolymerization reactions, as well as the thermal properties of the LVH-*co*-AN copolymers, were studied.

EXPERIMENTAL

Chemicals

The inhibitor in acrylonitrile (AN, Aldrich) was removed via an inhibitor removal column (Aldrich 30,631-2). 2,2′-Azobisisobutyronitrile (AIBN) (Eastman), DMSO (Aldrich) and methanol (Fisher) were used without further purification. Lactose-*O*-(*p*-vinyl)hydroxime (LVH) was synthesized with methods reported elsewhere[1]. The structure of LVH is shown below.



Copolymerization of LVH and AN

Copolymerization of AN and LVH was performed by using varying molar ratios of AN and LVH monomers. For 10/90 LVH/AN feed, 6.1 ml AN and 4.78 g LVH were added to 20 ml DMSO while being purged with nitrogen. Copolymerization was initiated by adding AIBN (0.0311 g) to the monomer mixture at 70°C for a designated period of time. The reaction was terminated by casting the polymer solution onto a glass plate and immersing the glass plate in methanol. The precipitated copolymer was rinsed with methanol to remove residual solvent. The copolymer was dried at 50°C under vacuum for 24 h. The conversion of monomers was calculated by the mass ratio of the copolymer product to the monomers in the feed. The

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oxygen contents of the copolymers were measured by elemental analyses (Midwest Microlabs) and used to calculate the molar fractions of LVH in the copolymers. The conversion of individual monomer was calculated by the mass ratio of the monomer existing in copolymer to the monomer in the feed.

Thermal property

Differential scanning calorimetry (d.s.c.) and thermal gravimetric analysis (TGA) of the copolymers were performed with a Shimadzu thermal analysis system (DSC 50 and TGA 50). The temperature and heat calibrations were performed using indium, zinc, and tin standards. The d.s.c. measurements were run under N_2 at 20°C min^{-1} heating rate to 500°C. For glass transition temperature determinations, the samples were first heated to 150°C to remove water, cooled, and then run at 10°C min^{-1} heating rate to 150°C.

Molecular weight

Molecular weights of the copolymers were analyzed by size-exclusion chromatography (SEC) equipped with triSEC GPC software. The SEC system consists of a Viscotek degasser (model DG-700), an Alcott HPLC pump (model 760), a Viscotek RALLS detector (model 600), and a Viscotek differential refractometer/viscometer detector (model 200). A Styragel HT linear column (for 2×10^3 to 10^7 dl g^{-1}) was used. The mobile phase was degassed HPLC-grade DMSO (Aldrich) containing 0.1 M LiBr (Fisher) flowing at 0.7 ml min^{-1}. Column and detector temperatures were maintained at 80 and 25°C, respectively. Copolymer solutions were made using the same solvent as the mobile phase. All solutions were filtered through 0.45 μm filters (Whatman) into a 100 μl injection loop. The column was calibrated using Dextrin standards. Peak parameters were calculated using a sucrose solution.

RESULTS AND DISCUSSION

Monomer conversion and copolymer composition

The copolymerization of acrylonitrile (AN) and lactose-*O*-(*p*-vinyl) hydroxime (LVH) behaves in typical free radical chain polymerization fashion. The effects of reaction time and initiator concentration were studied using a 95/5 AN/LVH monomer feed ratio. At a constant 2×10^{-3} [I]/[M] (mol/mol) concentration, the overall monomer conversion increases rapidly within the first 2 h, then becomes stable (*Figure 1a*). At a fixed 6 h reaction time, the total monomer conversion also increases with increasing initiator concentrations or [I]/[M] ratios (*Figure 1b*).

The effect of monomer feed ratio on the overall conversion of monomers is shown in *Figure 1c*. At the very low LVH concentrations, overall monomer conversions increase with LVH concentrations. The overall monomer conversions are around 70% when the LVH content in the monomer feeds is between 10% and 75%. The overall conversions of monomers appear to be independent of the monomer feed ratios within a wide range of LVH content.

Copolymer composition

The effects of reaction conditions on the compositions of copolymers and the conversion of the individual monomers were studied. Within the first hour of reaction, the conversion of LVH rapidly reaches 61.0%, while only 7.9% of AN is copolymerized (*Table 1*). After 4 h of reaction, 100% of LVH is consumed and the conversion of AN increases gradually. At an initiator concentration of 2×10^{-3}, the conversions of LVH and AN are 100% and 24%, respectively. With increasing initiator concentrations, the fractions of LVH in the copolymers decrease. The molar fractions of LVH in the copolymers are always higher than those in the monomer feed mixtures, implying a higher reactivity of LVH. This is also shown as a much higher LVH content in the copolymers with increasing LVH content in the monomer feeds (*Figure 2*).

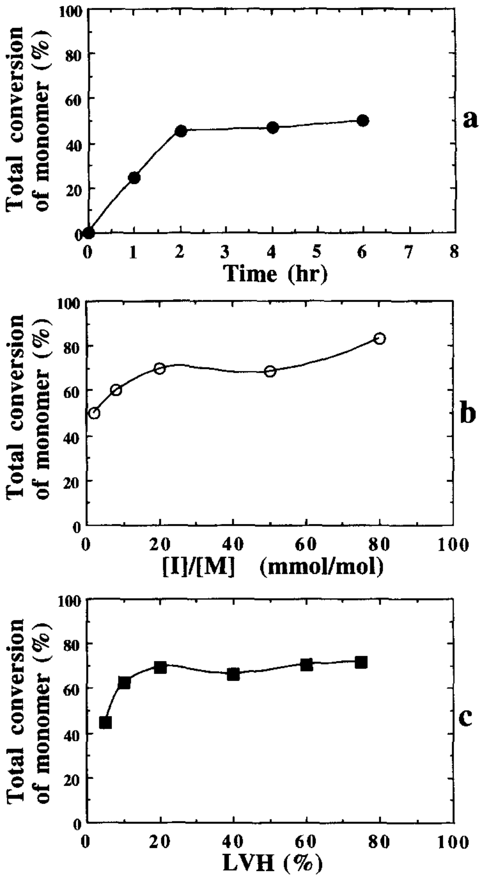

Figure 1 Total monomer conversion. (a) Effects of reaction time ([I]/[M] = 2 mmol mol^{-1}, $f_1 = 0.95$); (b) effects of initiator concentration (6 h, f_1 = 0.95); (c) effects of LVH content in monomer feed (6 h, [I]/[M] = 2 mmol mol^{-1})

Monomer reactivity ratio

Monomer reactivity ratios are often determined at low conversion of copolymerization based on the assumption that, for any given pair of monomers, the composition of the copolymer is a function of instantaneous feed only. However, because most copolymerization reactions are actually performed at high conversions, derivation of the monomer reactivity ratio at high conversion has been

Table 1 Effect of copolymerization conditions on monomer conversions and chain compositions

Reaction time (h)	[I]/[M] (mmol mol^{-1})	LVH (%)	Conversion of LVH (%)	Conversion of AN (%)
1	2	29.1	61.0	7.9
4	2	20.4	100	21.1
6	2	19.1	100	24.0
6	8	9.7	91.8	45.2
6	20	6.7	85.3	62.9

$T = 70°C$; $F_2 = 0.05$; [M] = 25 wt.%

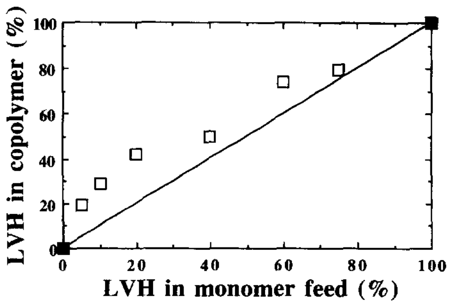

Figure 2 Relationship between LVH concentration on LVH content in copolymer (6 h, [I]/[M] = 2 mmol mol^{-1})

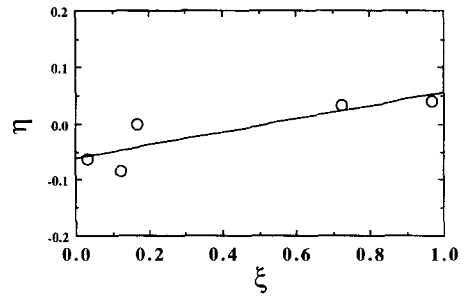

Figure 3 Reactivity ratio: plot of η *versus* ξ

extensively analyzed[11-14]. Among the methods proposed, the extended Kelen–Tüdös (Ex K–T) method has proven to be a very reliable one[15]. The Ex K–T equation[11] is expressed as:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \qquad (1)$$

where parameters ξ and η are defined as follows:

$$\xi = F/(\alpha + F) \qquad (2)$$

$$\eta = G/(\alpha + F) \qquad (3)$$

where parameters F and G are calculated from the experimentally obtained copolymer compositions F_1 and F_2 and the conversions of monomers ζ_1 and ζ_2, respectively.

$$F = Y/Z^2 \qquad (4)$$

$$G = (Y - 1)/Z \qquad (5)$$

$$Y = F_1/F_2 \qquad (6)$$

$$Z = \log(1 - \zeta_1)/\log(1 - \zeta_2) \qquad (7)$$

Parameter α in the Ex K-T equation is the geometric mean of F_m and F_M which are the lowest and the highest F values, respectively.

$$\alpha = (F_m F_M)^{0.5} \qquad (8)$$

In this study, the reactivity ratio (r_1 and r_2) of AN and LVH at high conversion (60%–70%) was determined with the Ex K-T method. The experimental and calculated data are included in *Table 2*. The plot of η and ξ is shown in *Figure 3*. With the intercepts at $\eta = 0$ and $\xi = 0$, the reactivity ratio r_1 and r_2 were calculated to be 0.0554 and 1.0975, respectively. It is therefore confirmed that the reactivity of LVH is much higher than that of AN.

*Molecular weight of AN-*co*-LVH copolymers*

The number average molecular weights of the AN-co-LVH copolymer are listed in *Table 3*. Under the reaction conditions studied, all M_n values are in the 10^5 range. At the same [I]/[M] ratio, the M_n appears to increase slightly as the LVH content in the monomer feed is raised from 5% to 20%. However, higher [I]/[M] ratio does lead to lower molecular weight, as expected.

*Thermal properties of AN-*co*-LVH copolymers*

D.s.c. thermal diagrams of the PAN and PLVH homopolymers as well as the An-*co*-LVH copolymers are shown in *Figure 4*. PAN homopolymer shows a sharp exothermic peak at 292.1°C. This exotherm relates to the cyclization reaction of nitrile groups. Although wide-angle X-ray diffractions of PAN fibers have indicated the existence of either single[17] or dual[18] glass transitions, no clear indication of glass transition of the PAN homopolymers is shown under this d.s.c. condition. The d.s.c. of PLVH shows a glass transition at approximately 125°C and a broader exotherm at 257.4°C, corresponding to the decomposition of the lactose moieties LVH[1]. The decomposition of the main chain of the homopolymers and copolymers occurs at temperatures exceeding 450°C.

The AN-*co*-LVH copolymer with only 3.25 mol.% LVH exhibit a glass transition associated with the LVH segments at 125°C. Copolymers with LVH contents between 28.7% and 79.7% exhibit glass transitions below 100°C. The lower transition temperatures of these AN-co-LVH copolymers may be due to the increased chain irregularity caused by the irregular helical conformation of AN segments[16], and the decreased number of hydrogen bonds between the hydroxyl groups in LVH.

The AN-*co*-LVH copolymers with 9.66 mol.% or less of LVH show two exotherms above 200°C. The lower-temperature peak is believed to be from the decomposition of LVH segments, and the higher-temperature peak is from the cyclization of AN segments. The shapes and positions of these two peaks vary with the copolymer compositions. With increasing LVH contents in the copolymers, the lower-temperature exotherm appears and increases in height. The higher-temperature peak shifts to a higher temperature before reducing drastically in height and eventually diminishing at 16.9 mol.% LVH. The changes in the higher-temperature peak indicate the reduction of nitrile cyclization in the copolymer as the LVH contents increase. This reduction may be due to the bulky side group in the LVH structure which increase the free volume, thus preventing nitrile cyclization. Cyclization of the nitrile groups is not observed when the LVH contents in the copolymers exceed 16.9%.

Table 2 Reactivity ratio calculation

f_1	F_1	Y	ζ_1	ζ_2	Z	F	G	η	ξ
0.90	0.7135	2.49	0.2741	0.9896	0.07	508.20	21.28	0.040	0.966
0.80	0.5798	1.38	0.3017	0.8745	0.17	46.1	2.20	0.034	0.722
0.60	0.5024	1.01	0.4692	0.6972	0.53	3.59	0.018	0.0008	0.169
0.40	0.2608	0.35	0.3869	0.7304	0.37	2.53	−1.73	−0.085	0.125
0.25	0.2035	0.26	0.5639	0.7253	0.64	0.62	−1.16	−0.063	0.034

$\alpha = (F_M F_m)^{0.5} = (508.20 \times 0.62)^{0.5} = 17.75$

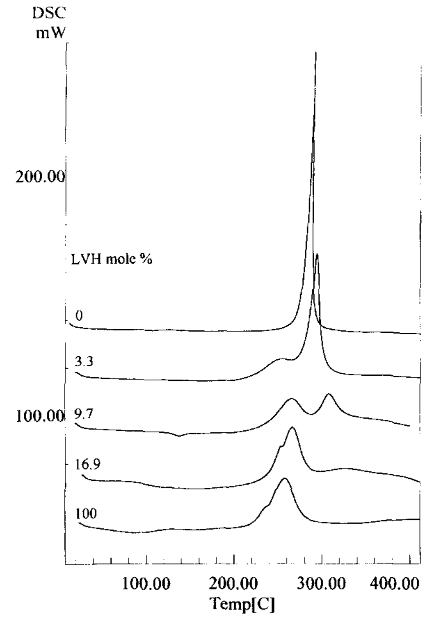

Figure 4 D.s.c. thermal diagrams of AN-*co*-LVH copolymers (20°C min^{-1})

CONCLUSION

With the extended Kelen–Tüdös method, the reactivity ratios of AN and LVH in solution copolymerization were determined to be 0.0554 and 1.0975, respectively. Because of the higher reactivity of the LVH monomer, the molar fractions of LVH in the copolymers are consistently higher than those in the monomer feed. When the LVH content in the monomer feed is less than 20%, the total monomer conversion and molecular weight of copolymer increase with increasing LVH content. In the early stage of copolymerization, the conversion of LVH is much higher than that of AN, and it reaches 100% in 2 h. When the LVH content is between 20 and 70%, neither the conversion nor the molecular weight depends on the feed ratios of the monomers. With longer reaction time and increasing initiator concentrations, the conversion and the content of AN in the copolymers increase gradually. A small amount of LVH in the copolymer chain reduces the cyclization of nitrile groups in AN segments. Cyclization of the nitrile groups in the copolymer is completely diminished when LVH contents in the copolymer is 16.9% and higher. The copolymers also exhibit lower glass transition temperatures than PLVH homopolymer.

Table 3 Number average molecular weight (M_n) of AN-*co*-LVH copolymers

AN/LVH feed ratio	[I]/[M]	M_n ($\times 10^5$)
95/5	2×10^{-3}	4.11
80/20	2×10^{-3}	8.82
40/60	2×10^{-3}	9.25
25/75	2×10^{-3}	6.03
5/95	2×10^{-3}	8.95
5/95	8×10^{-3}	3.48

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