Synthesis and Characterization of Low Molecular Weight Poly(maleic anhydride-co-vinyl acetate) Copolymers

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Abstract

As a part of a research on the development of polymeric textile finishing agents, polymerization of low molecular weight copolymers containing maleic anhydride residues have been studied. In order to obtain low molecular weight poly(maleic anhydride-co-vinyl acetate) copolymers, the feed ratio of the two monomers and the concentrations of initiator and chain transfer agent were varied in the copolymerization. The copolymers were characterized using GPC, NMR, FTIR, DSC, and TGA. Copolymers with molecular weights in the range 2,150 to 6,630 have been prepared and characterized. The hydrolysis of the anhydride groups of the copolymer in water is also discussed.

Introduction

Cross-linking of textile fibers is carried out to improve the dimensional stability and easy care properties. Formaldehyde based cross-linking agents are generally used to produce durable press fabric, but they produce small amounts of formaldehyde on hydrolysis. Since formaldehyde is classified as a carcinogen, various attempts have been made to produce formaldehyde free cross-linking agents. Polycarboxylic acids (PCAs), such as maleic acid, 1,2,3,4-butanetetracarboxylic acid (BTCA), etc., which crosslink cellulose via ester linkages have been reported [1]. Copolymers of maleic acid and itaconic acid whose molecular weight is approximately 10,000 have also been developed as polymeric ester forming cross-linking agents in Europe [2]. Since cross-linking agents must penetrate into the cotton fibers within a few minutes during the padding process, it was thought that lower molecular weights would be favorable for efficient penetration. Thus, in the copolymerization of maleic anhydride and vinyl acetate, that are known to have a tendency to form alternating copolymers, the feed ratio of the two monomers and the concentrations of AIBN initiator and dodecyl mercaptan chain transfer agent were varied in an effort to obtain low molecular weight poly(maleic anhydride-co-vinyl acetate) copolymers.

Experimental

Maleic anhydride, MAn, (Aldrich) and α-α'-azobisisobutyronitrile, AIBN, (Aldrich) was recrystallized from chloroform and methanol, respectively. Vinyl acetate, VAc, (Aldrich) was washed with 5% aqueous solution of NaOH to remove inhibitors, washed with distilled water until it became neutral, dried with $CaCl_2$, and fractionally distilled under reduced pressure. Toluene and diethyl ether were used as received. Copolymerization of MAn and VAc was carried out by adding MAn and VAc monomers and AIBN initiator to toluene, purging the reaction mixture with nitrogen and stirring under reflux at 70℃ for 4 hours. Dodecyl mercaptan was also added in the experiments where the effect of chain transfer agent on the molecular of the copolymer was studied. The copolymerization product was dissolved in warm toluene, precipitated in diethyl ether, filtered and dried in vacuum. The molecular weight of Poly(MAn-co-VAc) was measured on a Waters 2414 gel permeation chromatograph equipped with Styragel HR2, HR4 and HR5 columns (Waters). The measurement was carried out using THF as an eluent at 30℃, and the relative molecular weights compared with PS standards were determined. ^{1}H-NMR spectra of the copolymer in DMSO-d_6 were obtained on a Gemini 200 NMR spectrometer (Varian Co.), using TMS as an internal reference. Infrared spectra were obtained on a Perkin Elmer Spectrum GX FTIR spectrometer by scanning 12 times at a resolution of 2 cm^{-1}. The FTIR samples were prepared by dissolving the copolymer in acetone and casting on a CaF_2 window and drying. The thermal analyses of the copolymers were carried out on a TA 2100 DSC and TGA at heating rates of 10℃/min. The hydrolysis of the anhydride groups during dissolution in water and its regeneration on heating was studied using IR, DSC and TGA.

Results and Discussion

The effect of copolymerization conditions on the molecular weights of the copolymers are presented

in Table 1. Low molecular weights could be obtained by using high concentrations of initiator and chain transfer agent. The lowest molecular weights were obtained when both high levels of initiator and chain transfer agents were used.

Table 1. Copolymerization conditions and the resulting molecular weights of poly(MAn-co-VAc) copolymers

Sample	Monomer, initiator and chain transfer agent composition (% mol)				Molecular Weight GPC		
	MAn	VAc	AIBN	CT	Mn	Mw	Mw/Mn
1	1	1	0.005		4,860	12,000	2.47
2	1	1	0.01		4,520	11,700	2.58
3	1	1	0.02		4,240	11,000	2.59
4	1	1	0.04	0.03	2,890	7,080	2.45
5	1	1	0.04	0.06	2,520	6,220	2.47
6	1	1	0.04	0.09	2,270	5,450	2.4
7	1	1	0.04	0.12	2,150	4,720	2.19
8	1	1	0.001	0.014	6,230	10,900	1.75
9	3	7	0.001	0.014	6,630	17,300	2.61
10	1	9	0.001	0.014	4,780	7,460	1.55

The MAn:VAc mole ratio of the copolymers evaluated based on the areas of the characteristic peaks in NMR data was of ca. 1, in accordance with the reports that alternating copolymers are generally formed. The FTIR data in Figure 1 (a) shows the anhydride carbonyl bands at 1859 cm^{-1} and 1785 cm^{-1}, which disappear when the copolymer is dissolved in water then dried in vacuum. Poly(MAn-co-VAc) does not dissolve in water initially but gradually dissolves on hydrolysis of the anhydride groups to form carboxyl groups, (b). When hydrolyzed poly(MAn-co-VAc) is heated, the anhydride groups are again formed to some extent, even in the absence of a catalyst, (c).

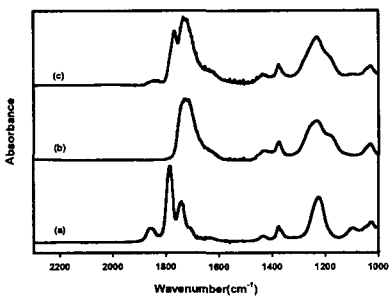

Figure 1. FTIR spectra of (a) poly(MAn-co-VAc), (b) hydrolyzed poly(MAn-co-VAc), (c) hydrolyzed poly(MAn-co-VAc) after 3 min. at 180℃.

The regeneration of anhydride groups on heating was further studied using DSC and TGA (Figures 2,3). Poly(MAn-co-VAc) does not exhibit DSC peaks up to 190℃, but the hydrolyzed sample shows a wide endotherm starting around 160℃ which is due to the elimination of water from two carboxyl groups to form anhydrides. The peak around 200℃ appears to be due to the decarboxylation of the anhydride groups as suggested in the literature [3]. Corresponding losses in the weights on elimination of water and decarboxylation can be seen in the TGA data.

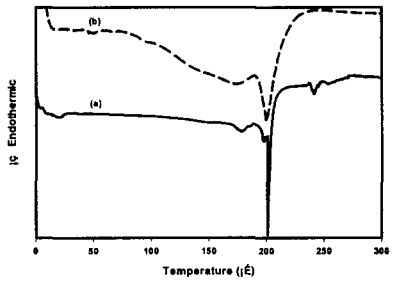

Figure 2. DSC thermograms of (a) poly(MAn-co-VAc) and (b) hydrolyzed poly(MAn-co-VAc).

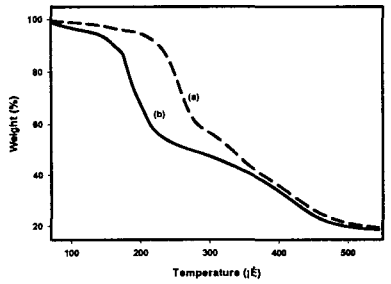

Figure 3. Thermogravimetric analysis of (a) poly(MAn-co-VAc) and (b) hydrolyzed poly(MAn-co-VAc).

Conclusions

Low molecular weight poly(maleic anhydride-co-vinyl acetate) copolymers may be obtained by increasing the concentration of initiator, chain transfer agent and by varying the monomer feed ratios. Poly(maleic anhydride-co-vinyl acetate) hydrolyzes when dissolved in water, but the anhydride functionality is partially regenerated when heated, even in the absence of a catalyst.

References

1. Q. Yang, J. Morisawa, Y. Ohtani, and K. Sameshim, Sen'I Gakkaishi **57**, 88-93 (2001).
2. C. Q. Yang, L. X. Shiqi, and Y. Jiang, *Textile Research J.*, **68**, 457-464 (1998).
3. J. J. Maurer, D. J. Eustace, and C.T. Ratcliffe, *Macromolecules*, **20**, 196-202 (1987).