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Cyclopolymerization of cinnamate ester derivatives of alkyl α-(hydroxymethyl) acrylates

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Summary

Three new monomers for cyclopolymerization were synthesized using phase transfer catalysis of ethyl α-(chloromethyl) acrylate (ECMA), t-butyl α-(bromomethyl) acrylate (TBBMA) and isobornyl α-(bromomethyl)acrylate (IBBMA) with cinnamic acid sodium salt. Bulk and solution polymerization at 70-80 °C using AIBN gave soluble cyclopolymers with Mn= 13650 and Mw= 36540 for the ethyl ester, Mn= 47700 and Mw= 86900 for the t-butyl ester and Mn= 3500 and Mw= 4650 for the isobornyl ester monomer. The ester polymerizabilities decreased with increasing substituent bulkiness. FTIR spectra showed ca 30 to 93% cyclic units depending on the concentration of the monomer used in polymerizations. DSC thermograms showed that alkyl group size had little effect on Tg's, with values of 151 °C, 156 °C, and 164 °C for the ethyl, t-butyl and isobornyl esters, respectively.

Introduction

Most work on cyclopolymerizations has focussed on symmetrical monomers having double bonds of comparable reactivities, although some unsymmetrical dienes having double bonds of different reactivities were also shown to cyclopolymerize (1). Although difunctional monomers generally give crosslinked polymers at high conversions, soluble cyclopolymers can be obtained at low conversions and/or in high dilution; eg, monomers containing cinnamate ester groups did undergo cyclopolymerization. Allyl α-methyl cinnamate cyclopolymerizations showed higher reactivity of the cinnamate over allyl double bonds, and gave polymers containing units resulting from intermolecular reactions of cinnamic acid and allylic double bonds plus five-membered lactone rings produced from intramolecular cyclization (1). Cyclopolymerization of cinnamyl methacrylate with benzoyl peroxide gave a polymer with both 5 and 6 membered rings (2). Vinyl trans-cinnamate polymerized to linear, soluble polymers containing γ-lactone rings but with 10-30% pendent unsaturation (3,4). The subject of the current article is synthesis and cyclopolymerization of cinnamate ester derivatives of alkyl α-(hydroxymethyl)acrylates containing ethyl, t-butyl and isobornyl groups to evaluate steric effects on cyclopolymerization.

Experimental

Ethyl α-(hydroxymethyl) acrylate (EHMA) (5), t-butyl α-(hydroxymethyl)acrylate

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(TBHMA) (6), TBBMA (7), ECMA (8) were prepared using the previously published procedures. Isobornyl α-(hydroxymethyl)acrylate (IBHMA) and IBBMA were prepared in a manner similar to TBHMA and TBBMA. Cinnamic acid was purchased from Aldrich and reacted with $NaHCO_3$ to prepare the acid salt. Monomers and polymers were characterized by ^{13}C NMR spectroscopy using a Bruker AC-200 spectrometer. Thermal analyses were done on a DuPont 9900 analyzer. Size exclusion chromatography (SEC) was carried out with THF solvent, American Polymer Standard columns of 500, 10^3, 10^4 and 10^6 A^0 packing, and polystyrene standards ($17.5x10^3$ to $3x10^6$ MW).

Representative Procedure for Synthesis of Cinnamate Esters

ECMA (6.2 g, 0.0418 m), cinnamic acid sodium salt (17.9 g, 0.105 m) and Aliquat 336 (Aldrich, 10 drops) in CH_2Cl_2 were added to a 100 ml round bottom flask and stirred at room temperature until all ECMA reacted as monitored by G. The solution was filtered and the CH_2Cl_2 evaporated; yd > 90%. Vacuum distillation gave the EHMA cinnamate as a viscous liquid. Solid TBHMA cinnamate was recrystallized from hexane (Tm= 40-41 ^{0}C). The IBHMA cinnamate was also a viscous liquid and was purified by passing it through a silica gel column using methanol as eluent.

General Polymerization Procedure

Monomer with AIBN in DMSO in a septum sealed test tube was subjected to three freeze-evacuate-thaw procedures and placed into a 70-80 ^{0}C oil bath. Polymers were precipitated into ether, reprecipated from CH_2Cl_2 into ether with vigorous stirring, and dried at 50 ^{0}C under vacuum. The ether soluble isobornyl ester polymer was precipitated into methanol.

Results and Discussion

The cinnamate ester derivatives of EHMA, TBHMA and IBHMA were synthesized as shown in Figure 1. Excess acid salt was used to convert all ECMA, TBBr and IBBMA to product as determined by G. Reaction times for synthesis of TBHMA cinnamate was very long (25 days) due to steric effect of the bulky t-butyl group. Changing solvent from CH_2Cl_2 to $CHCl_3$ and increasing temperature did not significantly decrease reaction times (20 days). Under the same conditions, the isobornyl cinnamate reaction took 5 days which showed that reactivity seems to depend not on the total bulkiness of the substituent but on the type of carbon attached to the substrate ester. Crude yields were very high (>90%).

The monomers were bulk and solution polymerized using AIBN. Table 1 gives polymerization conditions and results. During the polymerization of EHMA cinnamate in benzene, polymer precipitated; further polymerizations were carried out in DMSO. Bulk polymerization of EHMA cinnamate and TBHMA cinnamate monomers gave crosslinked polymers at high conversions. TBHMA and IBHMA cinnamate showed unexpectedly lower solution polymerizability than EHMA cinnamate; they did not give any polymer under the same conditions used for the EHMA cinnamate. Increasing the size of the alkyl substituent decreased polymerization rate due to steric hindrance. TBHMA and IBHMA cinnamate polymerizations were therefore done at high monomer concentrations and stopped at low conversions to prevent crosslinking. Similar behavior was seen during

polymerizations of allyl alkyl maleates where a decrease in polymerization rate and increase in selectivity of addition of the growing radical to the allylic double bond was observed on increasing the size of the alkyl substituent (1). The effect of substituent on polymerizability of cinnamate esters also relates to chemical shift difference of the vinyl carbons. In general, the larger the value of $\Delta\delta$, the lower the polymerizability (vida infra). $\Delta\delta$ values observed for EHMA, IBHMA and TBHMA cinnamate derivatives were 6.6, 7.1 and 8.1.

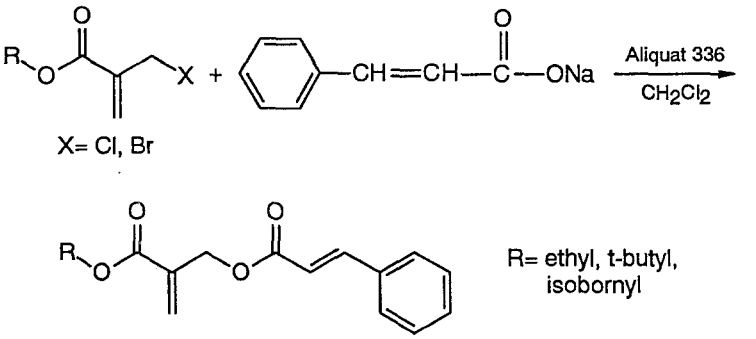

Figure 1. General synthetic schemes for cinnamate ester derivatives.

Table 1. Polymerization conditions and polymer characterization results

Cinn. Ester	[M]	[AIBN]	T (°C)	time (h)	con (%)	Mn	Mw	fc (%)
EHMA	1.94	0.054	74	44	32	3290	7469	-
EHMA	2.00	0.033	74	17	11	8890	16000	93
EHMA	2.00	0.033	74	44	28	13650	36540	80
EHMA	1.00	0.033	74	21	6	4810	5787	91
EHMA	4.20	0.134	82	21	42	6510	12955	86
TBHMA	1.83	0.088	75	48	0	-	-	-
TBHMA	13.4	0.334	75	7	10	16122	22223	51
TBHMA	5.20	0.130	74	24	<1	-	-	74
TBHMA	3.63	0.062	73	4	6	47685	86896	31
IBHMA	2.80	0.183	80	24	30	3500	4650	71
IBHMA	2.79	0.054	73	24	<1	-	-	-
IBHMA	13.3	0.540	85	20	10	3000	3660	-

Previous studies on 5-hexenyl radicals and 1-substituted derivatives showed that when the radical carbon is unsubstituted, 5-membered ring formation is favored while substitution favors six-membered rings, especially as the electron-withdrawing nature of the substituent increases (9). For example, 44% six-membered ring formation occurred for the 5-hexenyl radical containing one ethyl ester group at the radical carbon. Reactivity of the cinnamate ester double bond is very different from that of typical vinyl monomers; direct initiation and intermolecular propagation at cinnamate groups may be ignored. Polymerization of EHMA cinnamate should give 5 and/or 6 membered rings based on intermediate radical stabilities and ester group bulkiness (Figure 2). Since both the benzylic radical and that next to the carbonyl are stabilized, it is difficult to predict product structure.

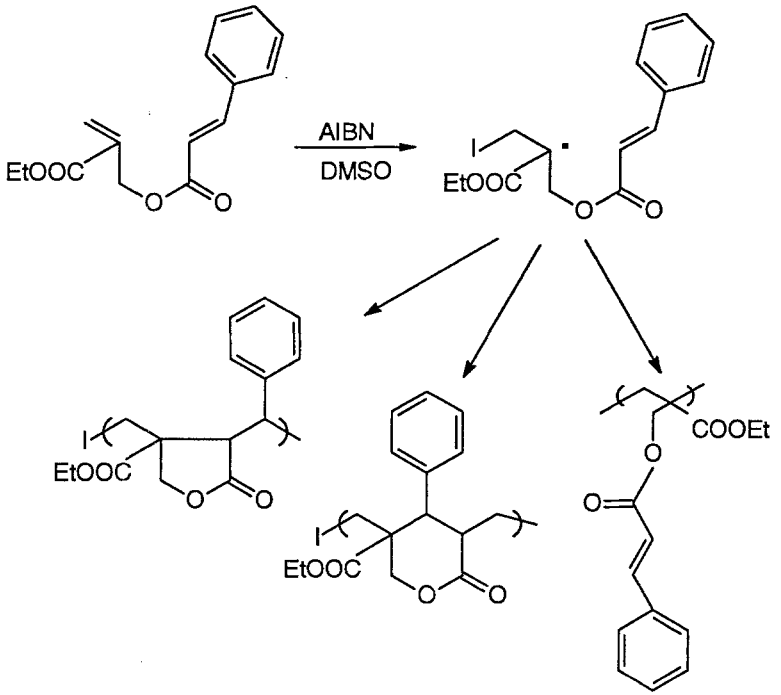

Figure 2. Intramolecular cyclization and intermolecular monomer additions

^{13}C NMR spectra of EHMA cinnamate monomer and polymer are shown in Figure 3. Structural assignments was made using DEPT 135 experiment. The peak at 62 ppm was assigned to the ethyl metylene carbon and the peak at 71 ppm to ring methylene groups. Peaks at 117 and 145 ppm correspond to unreacted pendent cinnamate double bonds. Determination of ring size using ^{13}C NMR was not possible due to the complexity of peaks in the backbone region (30-50 ppm). Two sets of peaks observed for all carbons may be due to cis/trans isomer formation during cyclopolymerization.[9] The ^{1}H NMR spectra of the EHMA cinnamate polymer obtained from solution polymerization surprisingly showed no pendant vinyl units. ^{1}H NMR spectra for TBHMA cinnamate and IBHMA cinnamate

polymers showed double bonds peaks but since these peaks were not well separated from the aromatic peaks, calculation of percent cyclization was not possible. However, the FTIR spectra of the polymers showed residual alkene groups at 1638 cm^{-1}, and the percent cyclic units (fc) were estimated from the ratio of peak heights for double bond versus carbonyl peaks. For EHMA cinnamate, the maximum cyclization reached was 93% with 7% residual double bonds. Comparison of FTIR spectra for bulk and solution polymerized TBHMA cinnamate samples showed that unreacted double bonds decreased with decreasing monomer concentration (characteristic of cyclopolymerizations) with the %-cyclization increasing from 30% for bulk to 75 % for solution polymerized sample. DSC analysis of the EHMA cinnamate polymer showed a glass transition temperature of 151 ^{0}C, while the TBHMA cinnamate polymer showed a Tg at 156 ^{0}C. When the latter was heated to 200 ^{0}C, an endotherm starting at 180 ^{0}C was observed due to loss of the t-butyl group. IBHMA cinnamate showed a Tg at 164 ^{0}C and thermal decomposition at 240 ^{0}C. Molecular weights for the TBHMA cinnamate polymer (Mn= 47700 Mw= 86900) were higher than the EHMA cinnamate polymer (Mn= 13650 Mw= 36540), probably due to a greater decrease in termination rate over the propagation rate. The low molecular weight of the IBHMA cinnamate (Mn= 3500 Mw= 4650) was due to the higher initiator concentration required for observable conversion in bulk.

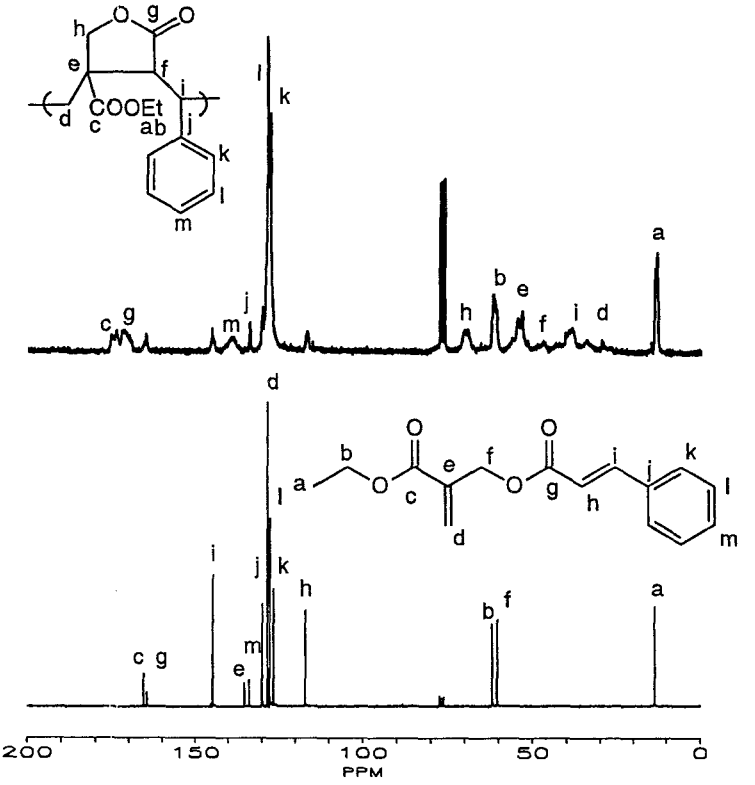

Figure 3. ^{13}C-NMR spectra for EHMA cinnamate monomer and polymer

Conclusions

Three monomers having two double bonds of widely different reactivities were tested for cyclopolymerizability. The bulkiness of the ester substituent decreased the polymerizability. Unexpectedly, cyclization efficiency of the reactions were relatively high and increased with decreasing monomer concentration.

Acknowledgement

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