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The copolymerization of substituted styrenes with α-methylene-γ-butyrolactone

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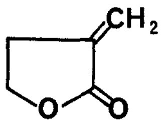
Summary

Copolymers of halogenated styrenes and α-methylene-γ-butyrolactone were synthesized in bulk via free radical initiation. The polymerizations, in most cases, proceeded rapidly to high conversion. The high conversions obtained necessitated the use of high conversion methods to calculate reactivity ratios. In all the copolymerizations the α-methylene-γ-butyrolactone proved to be the more reactive monomer.

Introduction

For some time we have been investigating the copolymerization of substituted styrenes with both common and unusual monomers in order to produce copolymers with unusual and/or unique properties (1-3). Particularly, we have been interested in comonomers that contain functionalities that would be capable of entering into post-polymerization reactions, crosslinking e.g. The reactive monomer investigated in this study, α-methylene-γ-butyrolactone (MBL) has a lactone functionaltiy that could enter into post-polymerization reactions via nucleophilic ring opening (4) e.g.:



α-methylene-γ-butyrolactone

The MBL is commerically available and has been the subject of previous investigations (5,6). However, information concerning copolymerization behavior was limited. We thought then, that it would be of interest to synthesize copolymers of MBL and investigate the range of properties that can be produced. As a first step it was necessary to characterize the reactivity of the various monomer pairs in copolymerization reactions by calculating reactivity ratios. This paper reports the results of these calculations.

Experimental

General

All solvents used in this study were purified by distillation from the appropriate drying agent. All the monomers used were purchased from Aldrich and were purified by distillation from CaH_2 immediately before use. Copolymer compositions were determined by comparing the areas of the appropriate signals in the ^{1}H-NMR spectra of the copolymers. The signal areas were measured by electronic integration. The spectra were obtained on 5-10% w/v solutions of polymer in $CDCl_3$ or d_6-DMSO with a Varian Gemini 300 FT NMR. Tetramethyl silane was used as an internal standard. Molecular weights were measured with a Waters 150 ALC/GPC equipped with 10^6, 10^5, 10^4, 10^3, 500 and 100 A microstyragel columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve.

Polymer Synthesis

The copolymers were synthesized by weighing the desired amounts of the comonomers into a clean, dry screw cap vial followed by 0.7 wt % AIBN. The monomer initiator solution was sparged with dry N_2 while cold (evaporation loss <1 wt %) and the vial was tightly sealed with a teflon lined cap. The vial was placed in a thermostated water bath at 65°C until a marked change in viscosity occurred, or in some cases, until the contents of the vial were semisolid, the time period for any such change to occur was usually very short. To terminate the polymerization the vial was removed from the bath and placed in cold water (10°C). When the vial and contents had cooled to approximately ambient temperature, 5-7 ml of CH_3OH were added to precipitate the polymer. The copolymer was purified by twice reprecipitating it from $CHCl_3$ or DMSO solution into CH_3OH. For some of the copolymerizations, additional purification was affected by extracting the sample with $CHCl_3$ (high MBL in feed) to remove any styrene homopolymer. For low MBL feed copolymers $CHCl_3$ extraction would have removed any MBL homopolymer as it is not soluble in $CHCl_3$ and would have been left behind. Samples were also extracted with acetone to remove MBL homopolymer. In all cases where these extractions were performed (samples 1, 3 and 5 in every series), the amount of extractable material was very small (0.3 wt % of total polymer).

For all the copolymers synthesized in this study the GPC traces were monomodal and the MWD's were fairly narrow. From these results we can state with some confidence that the polymers produced are true copolymer.

Results and Discussion

The monomer feed ratios, conversions and copolymer compositions are listed in Table 2.

The conversions in many of these polymerizations were quite high. Therefore, a nonlinear fit of the data using an integrated form of the Mayo-Lewis equation was used to find the reactivity ratios (7-9). This form of data treatment accounts for conversion in the calculation of r_1 and r_2. The results of these calculation are presented in Table 1.

TABLE 1

Reactivity Ratios

m_1	m_2	r_1	r_2	r_1r_2
MBL	MFS	0.57 ± .11	0.092 ± .02	0.052
MBL	PFS	0.84 ± .13	0.16 ± .03	0.14
MBL	MCS	0.51 ± .10	0.11 ± .02	0.056

The low values of r_1r_2 indicate that there is some alternating tendency in these copolymers. In order to obtain a better idea of the alternating tendency the average sequence lengths of MBL and the styrene were estimated using Pyun's (10) equations for some of the polymers synthesized in this study. The results are presented in Table 3.

The values in Table 3 confirm the preference of growing chains for the MBL monomer. The mean sequence length of MBL significantly increases with increased feed concentration of MBL. The mean sequence length of each styrene copolymer also increases with increasing feed concentration but not nearly as dramatically as the MBL sequence lengths.

Conclusions

Binary copolymers of α-methylene-γ-butyrolactone and some substituted styrenes were synthesized and reactivity ratios were calculated. The polymerizations were very rapid, yielding high conversions relatively quickly in most cases. The high conversions necessitated the use of high conversion methods to calculate the reactivity ratios. In all cases the MBL proved to be the more reactive monomer. The polymers with high proportions of MBL had different solubility behavior than those with low proportions of MBL.

TABLE 2

Feed Ratios, Conversions and Copolymer Compositions for MBL - Styrene Copolymers

Polymer	M_1	M_2[a]	M_f of M_1 in Feed	M_f of M_2 in Feed	Pzn Time (min)	Conv. (%)	M_n	M_w	M_f of M_1 in Copolymer	M_f of M_2 in Copolymer
MFS1	MBL	MFS	0.14	0.86	60	9.1	28800	50600	0.41	0.59
MFS2	MBL	MFS	0.39	0.61	60	1.5	33000	55800	0.51	0.49
MFS3	MBL	MFS	0.43	0.57	60	9.6	38500	63000	0.55	0.45
MFS4	MBL	MFS	0.58	0.42	60	1.0	44000	71000	0.64	0.36
MFS5	MBL	MFS	0.81	0.19	60	11.5	51000	76500	0.77	0.23
MFS6	MBL	MFS	0.86	0.14	60	7.0	-	-	0.83	0.17
PFS1	MBL	PFS	0.17	0.83	25	7.4	31500	55600	0.40	0.60
PFS2	MBL	PFS	0.27	0.73	25	15.7	41000	73000	0.48	0.52
PFS3	MBL	PFS	0.36	0.64	25	21.7	42000	75300	0.52	0.48
PFS4	MBL	PFS	0.46	0.54	25	32.2	47500	93000	0.55	0.45
PFS5	MBL	PFS	0.56	0.44	25	45.3	58600	114000	0.60	0.40
PFS6	MBL	PFS	0.73	0.27	25	80.3	-	-	0.82	0.18
MCS1	MBL	MCS	0.24	0.76	45	12.0	33000	57000	0.46	0.54
MCS2	MBL	MCS	0.46	0.54	45	39.6	39000	61000	0.53	0.47
MCS3	MBL	MCS	0.58	0.42	45	35.2	47000	76500	0.61	0.39
MCS4	MBL	MCS	0.74	0.26	45	21.4	51500	88000	0.71	0.29
MCS5	MBL	MCS	0.80	0.20	45	81.7	63000	97000	0.79	0.21
MCS6	MBL	MCS	0.87	0.13	45	97.0	-	-	0.83	0.17

a. MFS = m-fluorostyrene; PFS = p-fluorostyrene; MCS = m-chlorostyrene

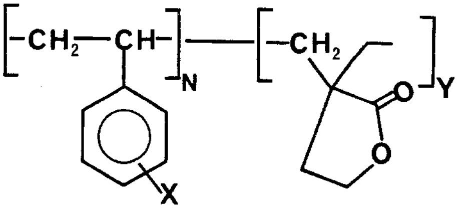
TABLE 3

Average Sequence Lengths

Polymer	m_1	m_2	μ_1	μ_2
MFS1	MBL	MFS	1.40	1.13
MFS3	MBL	MFS	1.70	1.08
MFS5	MBL	MFS	2.90	1.03
MFS6	MBL	MFS	3.80	1.02
PFS1	MBL	PFS	1.60	1.24
PFS3	MBL	PFS	1.90	1.15
PFS5	MBL	PFS	2.28	1.11
PFS6	MBL	PFS	4.90	1.04
MCS1	MBL	MCS	1.43	1.13
MCS3	MBL	MCS	1.80	1.07
MCS5	MBL	MCS	2.92	1.03
MCS6	MBL	MCS	3.49	1.02

a. μ_1 = mean sequence length of monomer 1 (MBL); μ_2 = mean sequence length of m_2

The highest MBL content polymers were not soluble in THF, which was the GPC solvent, which is why no molecular weights are recorded for these polymers. ^{1}H-NMR and IR spectroscopy strongly indicate that the polymer has the structure shown in Equation 1 i.e. the lactone ring is intact.



Equation 1

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