Polymerization of (*RS*)- and (*R*)-α-Methylene-γ-methyl-γ-butyrolactone

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ABSTRACT: The radical, anionic, and group-transfer polymerization of (*RS*)- and (*R*)-α-methylene-γ-methyl-γ-butyrolactone gave amorphous polymer with T_g's ranging from 211 to 220 °C. Polymer obtained from chiral monomer was much less soluble than that obtained from racemic monomer. Polymer obtained from chiral monomer via group-transfer polymerization was the least soluble, dissolving only in hot (230 °C) propylene carbonate. The ^{13}C (50.288 MHz) spectra of the polymers obtained from racemic monomers (Me_2SO at 100 °C) were nearly identical but were different from the spectra of the polymers obtained from chiral monomers, regardless of the method of polymerization. The peaks associated with the quaternary α-carbon were well enough resolved such that the single absorption for polymer obtained from chiral monomer could be assigned to the mm triad. The spectra of polymer obtained from racemic monomer showed predominantly mr and rr triads.

Introduction

The polymerization reactions and polymers obtained from α-methylene-γ-butyrolactones and -lactams are of interest because the monomers possess the structural characteristics and reactivity of methacrylates and methacrylamides, while the resulting polymers provide more rigid polymer chains than polymethacrylates or polymethacrylamides. The radical homopolymerization and copolymerization of *rac*-*N*-benzyl-α-methylene-γ-methyl-γ-butyrolactam have been reported.[1] In addition, an isomer of α-methylenelactone, γ-methylbutenolide (racemic), copolymerizes with styrene.[2] The spontaneous homopolymerizations of α-methylene-γ-butyrolactone, as well as its γ-methyl derivative, were reported coincident with its first synthesis; both these monomers were shown to undergo free radical polymerization.[3] Copolymerization of α-methylene-γ-butyrolactone takes place readily,[4,5] the reactivity ratios showing it to be a very reactive monomer with Q and e values (2.2 and 0.65) higher than those of methyl methacrylate.[5] Radical initiation appears to yield predominantly atactic polymer, while anionic polymerization apparently gives predominantly an amorphous, isotactic polymer.[6]

Both the atactic polymer and the stereoregular polymer show higher glass transition temperatures than poly(methyl methacrylate) and were difficultly soluble in common organic solvents. Because of the potential utility of optically active polymers,[7] the interesting solubility properties of the atactic and isotactic poly(α-methylene-γ-lactones), and the high solvent resistance, we undertook a study of the polymerization of both (*RS*)- and (*R*)-α-methylene-γ-methyl-γ-butyrolactone and the properties of the resulting polymers.

Results and Discussion

Monomer Synthesis and Polymerization. The synthesis of both racemic and chiral α-methylene-γ-methyl-γ-butyrolactone (**2**) was carried out by a known procedure[8] starting with either (*RS*)- or (*R*)-propylene oxide (**1**)[9] (Scheme I). The key step in the synthesis is the palladium-catalyzed carbonylation of 4-bromopent-4-en-2-ol. Thus, either racemic or chiral monomer could be obtained pure and in high yield by this procedure.

The polymerization of both (*RS*)- and (*R*)-α-methylene-γ-methyl-γ-butyrolactone was carried out by radical initiation (benzoyl peroxide) in benzene, by an anionic catalyst (butyllithium) in tetrahydrofuran or toluene, and by group transfer[10] [1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene initiator, tris(dimethylamino)sulfonium bifluoride catalyst in tetrahydrofuran (Table I)]. Polymerization in bulk with a benzoyl peroxide initiator or by UV irradiation gave a clear hard glass which contained ~20% of unreacted monomer. Higher conversions in bulk generally could not be achieved. The radical and anionic polymerizations in solution proceeded as expected, with no ring opening occurring in the anionic polymerization. Group-transfer polymerization of both racemic and optically active monomers took place readily at −78 °C when bifluoride was used as the catalyst, but the tetrabutylammonium fluoride catalyst did not provide good conversion at this temperature.

Polymer Properties. The racemic poly(α-methylene-γ-methyl-γ-butyrolactones) obtained under different reaction conditions had nearly identical solubility properties, dissolving in such solvents as acetone, acetonitrile, chloroform, dimethyl sulfoxide, dimethylformamide, and propylene carbonate at ambient temperature. Chiral lactone polymerized under radical conditions also was soluble in most of these solvents, with the exception of acetonitrile and chloroform (Table II). Polymers obtained from chiral lactone under anionic or group-transfer polymerization showed poor solubility in common organic solvents. The polymers obtained by anionic methods were soluble in dimethyl sulfoxide, dimethylformamide, and propylene carbonate, though only at elevated temperatures. The chiral polymer prepared by group-transfer polymerization was the least soluble and would dissolve completely only in hot (230 °C) propylene carbonate. None of these polymers showed any crystallinity by X-ray analysis. Regardless of the method of polymerization and the stereoregularity, the glass transition temperatures of these polymers were all approximately the same, ~215 °C, which was about 20 °C higher than the T_g for amorphous poly(α-methylene-γ-butyrolactone). Annealing these polymers above the glass transition temperature failed to develop any crystallinity.

Some information concerning the stereoregularity of these polymers was obtained through the NMR spectra. The most striking feature of both the ^{1}H and ^{13}C spectra was that the polymer obtained from racemic monomer gave nearly identical spectra, regardless of the method of polymerization. Futhermore, the spectra of the polymers obtained from chiral monomer were nearly identical, regardless of the method of polymerization, but were different from the spectra of the polymers obtained from racemic monomer.

Polymer obtained from racemic monomer (runs 1–3) showed a poorly resolved overlapping region at δ 2.11 with

Scheme I

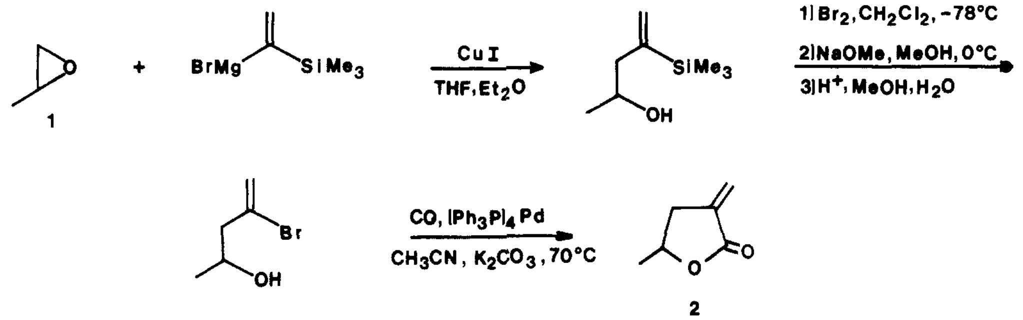
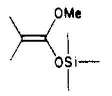
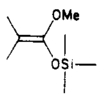


Table I
Polymerization of α-Methylene-γ-methyl-γ-butyrolactone

run	2	method	solvent (S)	[S]/[2]	init	[2]/[init]	cat.	T, °C	t, h	conv, %	$[\eta]^{25°C}$ CH$_3$COCH$_3$	$[\eta]^{25°C}$ Me$_2$SO
1	±	radical	C_6H_6	1	BPO	300		65	2	47	0.49	0.84
2	±	anionic	THF	9	BuLi	60		−78	2	86	0.26	
3	±	GTP	THF	6		65	bifluoride[a]	−78	24	70	0.22	
4	*R*	radical	C_6H_6	1	BPO	250		65	2	51	I[b]	1.06
5	*R*	anionic	THF	13	BuLi	60		−78	2	92	I	0.58
6	*R*	anionic	C_6H_5Me	10	BuLi	60		−78	44	85	I	0.75
7	*R*	GTP	THF	6		65	bifluoride[a]	−78	25	78	I	I

[a] 1 mol % of tris(dimethylamino)sulfonium bifluoride (based on initiator) was added as catalyst. [b] Insoluble.

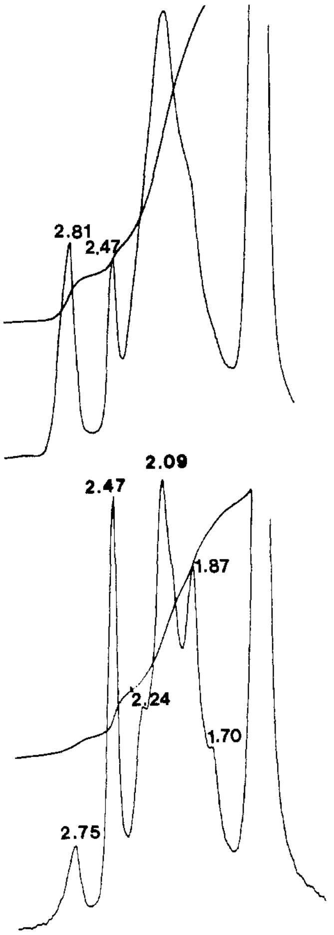


Figure 1. ^{1}H NMR spectra of polymer from racemic (top) and chiral (bottom) monomers.

a detectable upfield shoulder in the 100-MHz ^{1}H NMR spectrum at 160 °C in Me$_2$SO (Figure 1). Polymer obtained from chiral monomer showed a well-resolved doublet at δ 1.87 and 2.09 with downfield and upfield shoulders at δ 2.24 and 1.70, respectively. This is in contrast to the ^{1}H NMR spectra reported for poly(α-methylene-γ-butyrolactone),[6] in which no resolution was achieved (overlap at δ 2) for the backbone and ring methylene, both of which are adjacent to the quaternary carbon. This lack of resolution in poly(α-methylene-γ-butyrolactone) was attributed in part to coupling from the methylene (–CH$_2$O–) adjacent to the ring methylene. In the polymers obtained from chiral monomer, some resolution apparently results from the stereoregular environment and coupling of the ring methylene only to a methine proton.

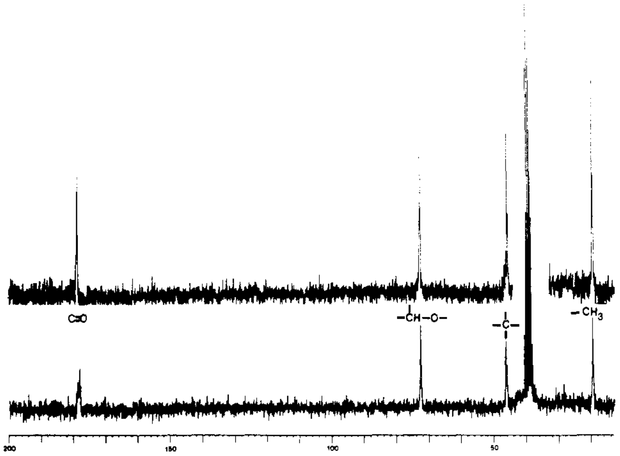


Figure 2. ^{13}C spectra of polymer from chiral (top) and racemic (bottom) monomers.

The proton-decoupled ^{13}C spectra of these polymers (50.288 MHz, 100 °C, Me$_2$SO, Figure 2) showed resolved peaks both in the carbonyl region, δ 178, and in the quaternary carbon region, δ 45–47. As in the case of poly(α-methylene-γ-butyrolactone), the methylene region was

Table II
Properties of Poly(α-methylene-γ-methyl-γ-butyrolactone)

	solubility[a]											
	CH_3CN	CH_3COCH_3	$CHCl_3$	Me_2SO			DMF		propylene carbonate			
run	25 °C	25 °C	25 °C	25 °C	100 °C	170 °C	25 °C	140 °C	25 °C	230 °C	$[\alpha]^{25}_D$, deg Me_2SO	T_g, °C
1–3	S	S	S	S			S		S		0	214–218
4	sw	S	sw	S			S		S		+0.425	220
5	I	I	I	I	sw	S	I	sw	I	S	+0.427	212
6	sw	sw	sw	sw	S	S	sw	S	sw	S	+0.415	218
7	I	I	I	I	sw	sw	I	sw	I	S	I	211

[a] S = soluble, I = insoluble, sw = swells.

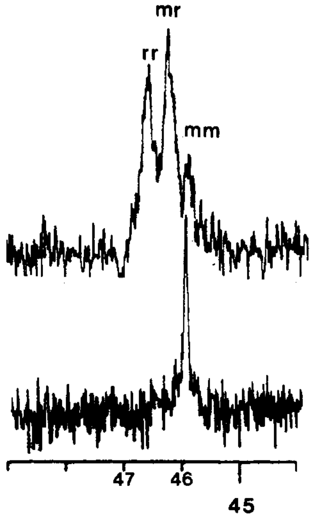


Figure 3. ^{13}C spectra, quaternary carbon, of polymer from racemic (top) and chiral (bottom) monomers.

poorly resolved and was overlapped by Me_2SO. Unlike poly(α-methylene-γ-butyrolactone), the carbonyl region showed resolved carbonyl at δ 178.74 and 178.67 for polymer prepared from racemic monomer and δ 178.67 and 178.87 for polymer obtained from chiral monomer.

Polymers obtained from racemic monomer showed peaks at δ 45.98, 46.32, and 46.64 for the quaternary carbon (Figure 3). In the spectrum of poly(α-methylene-γ-butyrolactone), peaks at δ 45.15, 45.3, and 45.58 were assigned tentatively to triad sequences, mm, mr, and rr, respectively.[6] This assignment was based on the fact that poly(α-methylene-γ-butyrolactone) obtained by anionic polymerization with phenylmagnesium bromide, which is known to yield highly isotactic poly(methyl methacrylate),[11] showed a spectrum rich in the upfield peak at δ 45.15, which was assigned to the mm triad. This assignment, rr, mr, mm, in order of increasing field strength, is the opposite of that for the quaternary carbon of poly(methyl methacrylate).[12]

If this peak assignment for the triads in poly(α-methylene-γ-butyrolactone) is correct, then the same assignment could be expected for poly(α-methylene-γ-methyl-γ-butyrolactone). Samples obtained from chiral monomer, having a single peak at δ 45.95 in the ^{13}C spectrum, suggested that an isotactic polymer (mm triads) was obtained. Polymer from racemic monomer showed a predominance of mr and rr triads at δ 46.30 and 46.58, respectively, with the peak at δ 45.95 nearly absent. In runs 1–3 the intensity of these two peaks (δ 46.30 and 46.58) was nearly equal, with that for the mr triad (δ 46.30) being slightly more intense.

The generation of isotactic polymer from chiral lactone, even in radical propagation, indicates that monomer placement is dictated by the chirality of the monomer. When models are examined (Figure 4) the preference for an isotactic polymer from chiral monomer becomes apparent. Approach of monomer to the growing end of the chain containing either of two conformations for the penultimate unit with respect to the end unit is shown. In both cases, the least steric approach is that which generates the mm triad. In the case of the polymerization of racemic monomer, addition of monomer of the same chirality as the polymer end generates the m dyad, while addition of monomer of the opposite chirality generates an r dyad, apparently with nearly equal facility from the racemic monomer pool.

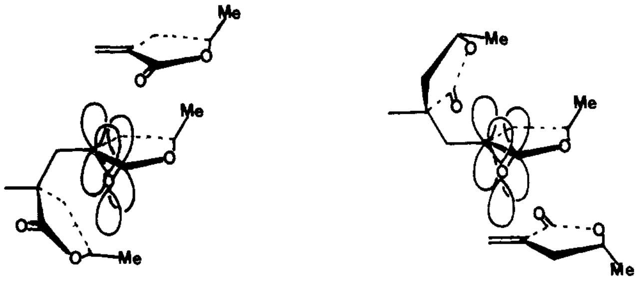


Figure 4. Approach of chiral monomer to chain end.

Experimental Section

Benzene, toluene, and tetrahydrofuran were freshly distilled under argon from sodium-benzophenone just prior to use. Acetonitrile was distilled under argon from calcium hydride. The butyllithium solution in hexane (1.6 M) was obtained from Aldrich. Benzoyl peroxide (Mallinckrodt) was purified by dissolving 15 g in 45 mL of chloroform and then precipitating it by pouring the chloroform solution into rapidly stirred petroleum ether (60–90 °C). The precipitate was removed by filtration and dried under reduced pressure (0.05 mmHg) at 25 °C for 1 h. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-2-propene was prepared from the methyl isobutyrate anion and trimethylsilyl chloride as described:[13] bp 50 °C (20 mmHg) [lit.[13] bp 35 °C (15 mmHg)]. This initiator was stored under argon. Tris(dimethylamino)sulfonium bifluoride was obtained from Du Pont.

Monomers. Both (*RS*)- and (*R*)-α-methylene-γ-methyl-γ-butyrolactone (2) were prepared as previously described[8] and were twice distilled before use: bp 45 °C (1 mmHg). Both racemic and chiral monomer were pure as shown by GLC. (*R*)-lactone, $[\alpha]^{25}_D$ +33.8°.

Radical Polymerizations. To 3.0 g (27 mmol) of lactone in 2.4 mL of benzene, under a nitrogen atmosphere, was added 22 mg (8.9×10^{-2} mmol) of benzoyl peroxide. The solution was heated to 60 °C for 2 h, after which the solution was cooled and diluted with methanol to precipitate the polymer. The precipitate was continuously extracted with ether for 15 h and then dried under reduced pressure. Run 4, Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.27; H, 7.20. Found: C, 64.00; H, 7.30 (no residue).

Anionic Polymerization. A solution of 2.0 g (18 mmol) of lactone in 14 mL of THF or toluene was introduced, under argon, into a polymerization flask (flamed under argon) fitted with a rubber septum. The solution was cooled to −78 °C and 0.18 mL (0.30 mmol) of 1.6 M butyllithium in hexane was added under argon. Within a few minutes the mixture gelled. Methanol (5 mL) was added to quench the reaction. The gel was broken into small pieces and was then continuously extraced with ether for 15 h. The polymer was dried under reduced pressure. Run 5, Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.27; H, 7.20. Found: C, 63.99; H, 7.33 (no residue).

Group-Transfer Polymerization. To a solution of 48 mg (0.27 mmol) of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and 2.7 μL (2.7×10^{-3} mmol) of a 1 M acetonitrile solution of tris(dimethylamino)sulfonium bifluoride in 8.7 mL of THF under argon at −78 °C in a reaction flask (flamed under argon) was quickly introduced 2.0 g (18 mmol) of lactone. Within a few minutes, the reaction mixture became a gel. After 24 h, the gel was allowed to warm to ambient temperature. Methanol was added and the gel was broken into small pieces by stirring. The polymer was continuously extracted with ether for 15 h and then dried under reduced pressure. Run 7, Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.27; H, 7.20. Found: C, 64.04; H, 7.29 (no residue).

NMR. ^{1}H NMR spectra were taken on Me_2SO polymer solutions at 160 °C with a JEOL FX-100 spectrometer at 100 MHz. ^{13}C spectra were obtained on Me_2SO solutions containing 7.5 wt % polymer (runs 1–4 and 6) or 5 wt % polymer (runs 5 and 7) at 100 °C using an IBM WP-200 (50.288 MHz) with a broad-band variable-temperature 10-mm probe. Generally, 20000–40000 scans were accumulated, depending on the sample concentration and the region of the spectrum observed.

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Swelling of Ionic Gels: Quantitative Performance of the Donnan Theory

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ABSTRACT: This study investigates the quantitative consistency of the Donnan theory of swelling of weakly charged ionic gels. Instead of the usual a priori assumptions about the volume dependence of the swelling pressure of the neutral network, this function is obtained as one of the results of the study. The theory is applied to predict quantitatively the swelling of a polyacrylamide–acrylic acid copolymer gel as a function of ionic composition of the solvent. No free parameters are used. As long as no multivalent ions are involved, the changes in swelling and swelling extrema occur exactly at predicted ion concentrations in the solutions. The extent of swelling is also satisfactorily predicted. In solutions containing divalent cations, significant quantitative discrepancies between the theory and the experiment are observed, but qualitative features are adequately described.

1. Introduction

The interest in ionic gels has been revived since the observation of the phenomenon of phase transition in such systems by one of the authors.[1] A partially hydrolyzed acrylamide gel can change its volume discontinuously when the solvent composition is continuously varied. Charged groups attached to the network play an essential role in this phenomenon.[2-4] The transition can be induced by changing the pH of the solvent, by changing salt concentrations, or by applying an electric field.[2,5,6] A complete description of such phenomena depends on an understanding of the role of charges in the system.

Theories on swelling of ionic gels are reviewed in ref 7. Most of the theories tend to be quite complex, attemping to combine the description of the contractile force of the network (network swelling pressure) and the electrostatic interactions (ion swelling pressure) in one model. Such theories contain many free parameters and their experimental verification is therefore difficult.

The simplest of the theories attributes the ion swelling pressure to the difference between the osmotic pressure of freely mobile ions in the gel and in the outer solution.[8-10] The distribution of the ions between the gel and the outer solution is obtained from Donnan equilibrium. Within this theory the ionic forces depend only on the ionic composition of the solvent and on the concentration of fixed ionizable groups in the gel but not on the properties of the neutral network.

We will take advantage of this simplification and proceed according to the following concept. First we use the ion pressure to swell gels in a desired extent. We do perform the experiments using acrylamide–acrylic acid copolymer gels in one solvent having a simple ionic composition. We adjust the ion swelling pressure by varying the amount of fixed charges in the gel. This pressure, which can be calculated under the assumption of the validity of the Donnan theory, is equal to the negative of the swelling pressure of the neutral network at the given equilibrium volume.

We next use the data on the network thus obtained to predict quantitatively the swelling of a gel in solutions with varying ionic composition. When the prediction turns out