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Poly(α-methylene-γ-butyrolactone) Synthesis, Configurational Structure, and Properties

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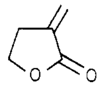
ABSTRACT: α-Methylene-γ-butyrolactone (α-MBL, I) has been shown to be a reactive vinyl monomer capable of both free-radical and anionic polymerization. High-resolution ^{13}C NMR was found to be of particular value in determining the configurational microstructure of the polymers using the quaternary carbon as the stereochemical probe. Poly(α-MBL) from free-radical initiation was found to be atactic with slight preponderance of syndiotactic placements ($P_m \simeq 0.37$) with very little dependence of the tacticity on the temperature of the polymerization. Anionic polymerization with PhMgBr in toluene and 9-fluorenyllithium in THF at −78 °C yielded polymers that on the basis of present assignments are predominantly isotactic (P_{mm} = 0.73, 0.75, respectively). Poly(α-MBL) from free-radical polymerization is amorphous and has a high glass transition temperature (T_g = 195 °C) and solvent resistance, characteristic of structural rigidity of the chain segments.

α-Methylene-γ-butyrolactone[1] (α-MBL, I) is the simplest member of a class of naturally occurring sesquiterpene lactones which have become, in recent years, the subject of considerable research interest[2] owing to their demonstrated cytotoxicity and tumor-inhibitory properties.[3] α-MBL itself, often referred to as Tulipalin A,[4] occurs in the common tulip, Tulipa Gesneriana L, as the glucoside of the corresponding γ-hydroxy acid. Since the initial report of Jones et al.[5] on the synthesis of α-MBL, other methods have been described for the synthesis of both α-MBL and related compounds containing the α-methylene-γ-lactone structural moiety of interest to medicinal chemists.[6] However, very little attention has been paid to the potential of α-MBL as a reactive, polymerizable monomer, particularly in view of the fact that the monomer possesses structural features similar to those of methyl methacrylate (II, MMA). Except for a patent by McGraw,[7] very little is known regarding the polymerization characteristics of α-MBL or the structure and properties of the polymer. α-MBL may be considered as an example of a more general class of *exo*-methylene cyclic monomers capable of polymerizing via the double bond. Methylene cycloalkanes,[8] however, are known to polymerize reluctantly by cationic initiators yielding low molecular weight polymers. 2-Methylenetetrahydrofuran[9] is another example known to polymerize cationically and was reported to yield predominantly isotactic polymer[10] in hydrocarbon solvents.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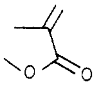
II

Since the growing chain end in the polymerization of α-MBL consists of a cyclic moiety, as in the above examples, it was of interest to determine the effect of the lactone ring on the propagation and stereochemistry of the chain. In view of the structural similarity to MMA, it was also of interest to determine whether α-MBL would polymerize by anionic initiation without ring opening. In this paper, some aspects of the free-radical and anionic polymerization characteristics of α-MBL, as well as the stereochemical configuration and other pertinent properties of the polymer, are discussed.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (Aldrich), *n*-butyllithium (1.6 M in hexane, Foote Mineral Co.), γ-butyrolactone (Matheson Coleman and Bell), diethyl oxalate (Aldrich), di-*tert*-butyl peroxide (Polysciences, Inc.), paraformaldehyde, and sodium ethoxide (Aldrich) were all of reagent grade and were used as supplied.

Tetrahydrofuran and toluene were distilled from 0.5% calcium hydride (Ventron). Fluorene (Aldrich) was recrystallized from cyclohexane and dried under vacuum just prior to use.

α-Methylene-γ-butyrolactone (α-MBL, I). I was synthesized from γ-butyrolactone (III) in an overall yield of ~60% according to the reaction scheme, shown below, reported by Ksander et al.[11] The procedure was, however, modified such that the intermediate α-ethoxalyl-γ-butyrolactone (IV) was not isolated, and instead its sodium salt was reacted directly with formaldehyde using THF as solvent.

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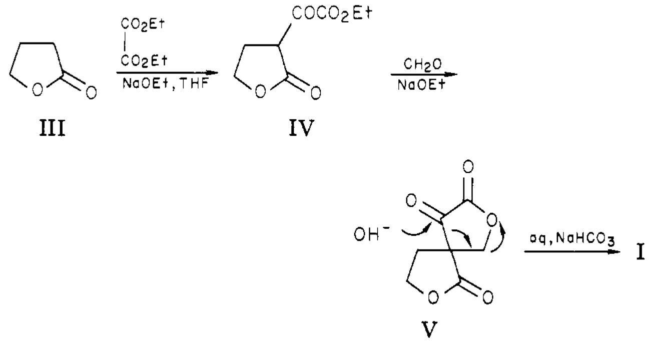


To a well stirred solution of sodium ethoxide (102 g, 1.5 mol) in THF (1 L) was added diethyl oxalate (220 g, 1.5 mol) followed by dropwise addition of γ-butyrolactone (130 g, 1.5 mol) while maintaining the temperature at 15 °C. After the addition was complete, the stirring was continued for 1 h at 15 °C and then overnight at room temperature. The sodium salt of α-ethoxalylbutyrolactone precipitated as a white solid. Into the slurry of sodium salt so obtained was then bubbled with stirring formaldehyde gas generated by cracking paraformaldehyde (60 g, 2 mol) in a separate flask under a slow nitrogen sweep. The temperature of the reaction was maintained below 45 °C. At the end of the reaction, a colorless solution with a suspension of some reformed paraformaldehyde gel was obtained. A portion of the solvent was distilled off under reduced pressure, and the contents were diluted with excess diethyl ether (2 L) and filtered. The precipitate was extracted repeatedly with ether. The combined ether extracts and the filtrate were stirred with 500 mL of saturated aqueous $NaHCO_3$ for 1 h at room temperature. The ether layer was then separated, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The oily residue was distilled under vacuum from 100 ppm hydroquinone added as an inhibitor. α-MBL distilling at 50–53 °C (0.5 mm) [lit. 86 °C (10 mm)] was obtained in 60% yield. It was redistilled using a fractionating column to collect the pure monomer at 50 °C (10 mm) (>99.7% by GC): $n^{25}{}_{D}$ -1.4560; ^{1}H NMR ($CDCl_3$) δ 5.65 (t, 1 H, J = 3 Hz), 6.18 (t, 1 H, J = 3 Hz), 4.35 (t, 2 H, J = 8 Hz), 3.0 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ (from Me_4Si) 170.07 (>C=O), 133.35 (C=), 121.05 (=CH_2), 64.80 (-CH_2O-), 26.62 (-CH_2-). The monomer must be stored in a refrigerator in order to prevent slow polymerization which occurs upon standing at room temperature or exposure to light.

Poly(α-methylene-γ-butyrolactone). (a) Free-Radical Polymerization. In a typical polymerization experiment a solution of AIBN (e.g., 0.5%) in the monomer was charged into a polymerization tube. The tube was repeatedly degassed on a vacuum manifold by freeze–thaw cycles and finally sealed under nitrogen. The tube was placed in a constant temperature bath (e.g., 60 °C) for a specified period of time (e.g., 24 h). At the end of polymerization, the transparent solid plug of the polymer was removed from the tube, ground to a fine powder in a freezer mill, and extracted with methylene chloride in a soxhlet apparatus to remove the residual monomer. Alternatively, the polymer was dissolved in dimethylformamide (DMF) or dimethyl sulfoxide (Me_2SO) and precipitated into methanol. The final conversions were typically ~67% at 60 °C. Polymerization at 140 °C was similarly conducted using di-*tert*-butyl peroxide as the initiator. Photopolymerization at 25 °C was conducted on a thoroughly degassed monomer sample containing 0.1% AIBN in a sealed polymerization tube. The tube was then exposed to a 75 W GE spot lamp for ~100 h. The final conversion was 58%.

(b) Anionic Polymerization. A solution of 9-fluorenyllithium initiator was prepared by refluxing a mixture of recrystallized fluorene (0.2 g; 1.2 mmol) and n-butyllithium (0.8 mL of 1.6 M solution in hexane; 1.28 mmol) in anhydrous tetrahydrofuran (50 mL) under nitrogen for 1 h. The resulting bright orange colored solution was then cooled to -78 °C, freshly distilled α-MBL (5 g) was added to the cold initiator solution by a hypodermic syringe, and the contents were stirred for 6 h at -78 °C under nitrogen. The precipitation of the polymer ensued within a few minutes of the reaction. The slurry of the polymer was poured into excess methanol followed by filtration, washing, and drying. Poly(α-MBL) was obtained in nearly quantititive yield.

9-Fluorenyllithium in toluene was similarly prepared but the initiator was obtained as a slurry due to its limited solubility in this solvent. The polymerization of α-MBL in this medium was found to be rather slow at -78 °C, e.g., <10% conversion in 6.0 h. The polymerization at 0 °C, however, yielded nearly a quantitative amount of polymer in 6 h.

Phenylmagnesium bromide was prepared as a 1 M solution in dry diethyl ether by refluxing pure bromobenzene with a slight excess of magnesium metal and a trace of iodine as catalyst. A solution of α-MBL (5 g) in dry toluene (50 mL) was cooled to -78 °C and treated with 2.5 mL of the phenylmagnesium bromide solution (2.5 mmol) under nitrogen. An immediate precipitation of the polymer occurred; however, the overall yield of the polymer was only 40% in 6 h.

Methods. Inherent viscosities of poly(α-MBL) were determined in DMF or Me_2SO at 25 °C. High molecular weight poly(α-MBL) was found to be soluble only in Me_2SO.

TGA analysis of the polymers was performed on a Cahn Electrobalance or duPont 951 TGA instrument at a heating rate of 10 °C/min in argon. DSC analysis was performed on a duPont 990 DSC instrument at a heating rate of 20 °C/min in argon.

Proton-decoupled ^{13}C NMR spectra were recorded in the pulsed fourier transform mode on a Varian CFT-20 (20 MHz) or Bruker HX270 (67.8 MHz) spectrometer. Typically, a solution of 15% (w/w) poly(α-MBL) in Me_2SO-d_6 was examined at 100 °C. The spectral parameters used for the CFT-20 instrument typically consisted of: 4096 or 8192 data points at 4000-Hz sweep width, a total of 24 000 to 113 900 cumulative transients, pulse width of 10 μs, and a noise band width of 1000 Hz. Peak areas were measured where possible by using a duPont 301 Curve Analyzer.

^{1}H NMR spectra were recorded on a Varian T-60 or HA-100 instrument. Anionically polymerized samples of poly(α-MBL) were examined for crystallinity on a Norelco X-ray diffractometer.

Alkaline Hydrolysis of Poly(α-MBL). Poly(α-MBL) (1 g) was suspended in 20 mL of 5 M aqueous KOH solution and heated with stirring for 48 h at 100 °C. The transparent gellike suspension so obtained was centrifuged, washed with methanol, and dried. The potassium salt of poly(α-methylene-γ-hydroxybutyric acid) (VI) so obtained in quantitative yield was highly hydrophilic but insoluble in water. IR (KBr disk) showed the characteristic carboxylate band at 1580 cm^{-1} and the absence of the lactone carbonyl at 1765 cm^{-1} indicating completion of hydrolysis. Acidification of a suspension of VI in water caused complete lactonization to poly(α-MBL).

Pyrolysis of Poly(α-MBL). Poly(α-MBL) (5 g) was heated at 360 °C under vacuum (1 mm), and the vapors were condensed in a dry ice trap. The liquid pyrolysis product consisted of α-MBL (I) as the major component as characterized by ^{1}H NMR.

Hydrazinolysis of Poly(α-MBL). Poly(α-MBL) (1 g) was refluxed with hydrazine hydrate (20 mL) for 3 h under nitrogen, and the clear solution so obtained was poured into excess methanol. Poly(α-methylene-γ-hydrpxybutyric acid hydrazide) (VII) was filtered and dried (100%) (IR band at 1660 cm^{-1}, characteristic of -CONH-). The polymer is readily soluble in water.

Results and Discussion

Polymerization Characteristics of α-Methylene-γ-butryolactone. α-MBL may be visualized as a cyclic analogue of methyl methacrylate (II), and, hence, the free-radical polymerizability is expected to be similar. The propagating free radical in both cases is stabilized by the adjacent >C=O group. α-MBL was indeed found to polymerize quite readily with such free-radical generators as AIBN, *tert*-butyl peroxide, and light. The bulk polymerization with AIBN at 55 °C shows the typical rate behavior shown in Figure 1. An estimate of the overall polymerization rate constant k from the following equation, initial rate (% conversion h^{-1}) = $k[AIBN]^{1/2}$, gave an average value of 190 at 55 °C which is comparable to the value of 128 reported for the bulk polymerization of MMA[12] at 60 °C. The somewhat higher reactivity of α-MBL thus indicated is consistent with our results of copolymerization reactivity[13] with MMA, viz., the observed

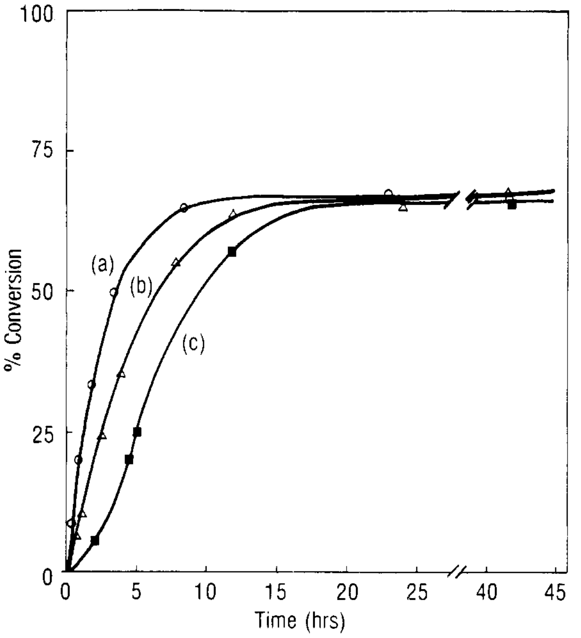


Figure 1. Bulk polymerization of α-methylene-γ-butyrolactone with AIBN as initator at 55 °C (I_0 = (a) 1.5 × 20^{-2} M, (b) 5.6 × 10^{-3} M, (c) 2 × 10^{-3} M, respectively).

values of $r_{\alpha\text{-MBL}} = 1.67$ and $r_{\text{MMA}} = 0.6$.

The degree of polymerization showed a steady increase with decrease in the initiator concentration (Table I, polymers no. 1–6) and in general was found to follow the relationship $\eta_{\text{inh}} \propto [\text{AIBN}]^{0.35}$ for the bulk polymerization at 60 °C.

The most characteristic feature of the bulk polymerization of α-MBL was, however, the apparent limiting final conversion obtained at a given temperature, e.g., 68% at 55 °C or ~72% at 60 °C (Figure 1 and Table I). The polymerization stops at this conversion as the polymerization mixture becomes a transparent, hard glass. DSC analysis of poly(α-MBL) indicated a rather high glass transition temperature for the polymer, viz., T_g = 195 °C, and a typical polymer sample containing ~21% monomer showed a T_g of 61 °C by DSC. As the T_g of the monomer–polymer mixture approaches the temperature of polymerization, translational diffusion of monomer and segmental diffusion of chain ends become extremely slow, and hence polymerization stops at the limiting conversion. Solution polymerization in Me_2SO does indeed lead to higher conversions (Table I). Anionic polymerization of α-MBL was considered feasible because its propagating carbanion, as is the case with the structurally similar MMA, is capable of resonance stabilization by the adjacent carbonyl group. However, nucleophilic ring opening of the lactone may also occur although γ-butyrolactone itself is known to be quite resistant to homopolymerization. α-MBL was found to polymerize by typical anionic initiators used for the polymerization of MMA,[14,15] viz., phenylmagnesium bromide and 9-fluorenyllithium. In a polar solvent such as THF, the polymerization proceeded quite readily with 9-fluorenyllithium at −78 °C with quantitative yield of the polymer which precipitated out of the reactor medium (Table I). In toluene, however, 9-fluorenyllithium is only slightly soluble, and accordingly the polymerization was very slow at −78 °C but occurred quite readily at 0 °C. Ion pair solvation, thus, seems to play a significant role in the polymerizability of α-MBL. However, the effect of the impurities, the polarity of the solvent temperature, and the nature of the initiator on the anionic polymerization of α-MBL must be studied in more detail to understand the mechanism of propagation. It is important to note, however, that the polymer obtained by anionic initiation, in general, showed no evidence of lactone ring opening, and the polymerization occurred only via the double bond since the IR was very similar to that of the free-radical-initiated polymer with strong lactone carbonyl absorption at 1765 cm^{-1}. The microtacticities of the polymers were, however, found to be quite different from each other, as shown by the high-resolution ^{13}C NMR spectroscopy.

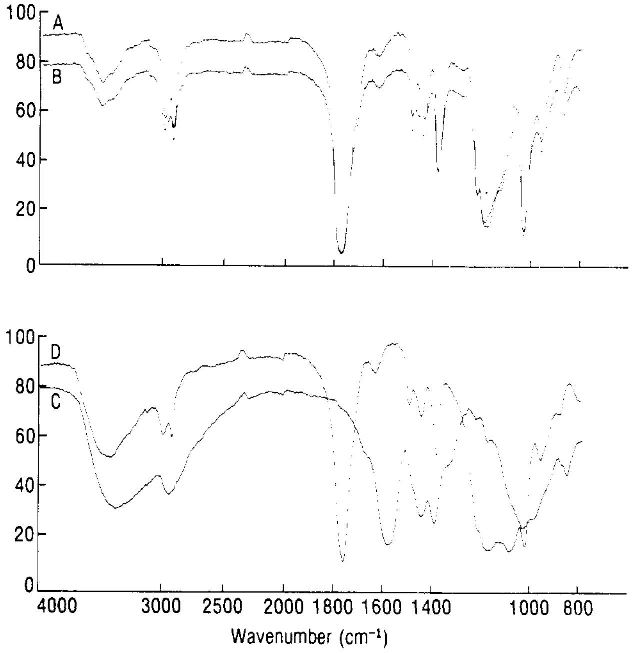


Figure 2. Infrared spectrum (KBr disk) of (A) poly(α-MBL) polymerized by AIBN at 60 °C, (B) poly(α-MLB) polymerized by 9-fluorenyllithium in THF at −78 °C, (C) product of alkaline hydrolysis of poly(α-MBL), and (D) same as (C) only acidified at 25 °C.

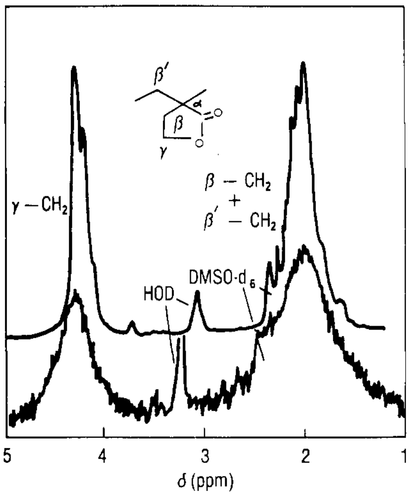


Figure 3. ^{1}H NMR (100 MHz) of poly(α-methylene-γ-butyrolactone) in $\text{Me}_2\text{SO-}d_6$ at 25 °C (bottom) and 150 °C (top).

Stereochemical Configuration of Poly(α-MBL). In analogy to most vinyl polymers, the poly(α-MBL) chain is expected to consist of isotactic (m) and/or syndiotactic (r) placement of successive monomer units to varying

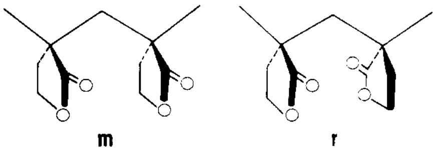


Table I
Polymerization of α-Methylene-γ-butyrolactone

polymer no.	initiator	$[I]_0/[M]_0$, % (w/w)	polymerization conditions	yield, %	η_{inh}
1	AIBN	0.05	bulk, 60 °C, 48 h	72	1.04
2	AIBN	0.1	bulk, 60 °C, 48 h	75	0.79
3	AIBN	0.2	bulk, 60 °C, 48 h	75	0.64
4	AIBN	0.5	bulk, 60 °C, 48 h	70	0.6
5	AIBN	0.75	bulk, 60 °C, 48 h	70	0.4
6	AIBN	1	bulk, 60 °C, 48 h	72	0.36
7	AIBN	1	$[M]_0$ = 2.7 M in Me_2SO, 60 °C, 72 h	93	0.8
8	AIBN, light[b]	0.1	bulk, 25 °C, 100 h	58	2.97[c]
9	t-Bu_2O_2	0.5	bulk, 140 °C, 24 h	82	
10	C_6H_5MgBr	0.49[d]	$[M]_0$ = 1 M in toluene, −78 °C, 6 h	40	
11	9-fluorenyllithium	2.35[d]	$[M]_0$ = 1 M in toluene, −78 °C, 6 h	8	
12	9-fluorenyllithium	2.35[d]	$[M]_0$ = 1 M in toluene, 0 °C, 6 h	95	0.16
13	9-fluorenyllithium	2.35[d]	$[M]_0$ = 1 M in THF, −78 °C, 6 h	100	0.1

[a] Measured in DMF at 25 °C. [b] 75 W GE spot lamp placed about 10 in. from the polymerization tube. [c] Due to its insolubility in DMF, it was measured in Me_2SO at 25 °C. [d] Mol %.

extent depending upon the conditions of polymerization. It is generally possible to obtain information regarding configurational sequences in a polymer chain (diads, triads, etc.) by the application of high-resolution NMR. ^1H NMR (100 MHz) of poly(α-MBL) in Me_2SO-d_6 (Figure 3) showed only two broad, poorly resolved peaks at δ 2 (β-CH_2 and β'-CH_2) and δ 4.2 (γ-CH_2) even at 150 °C. The overlapping chemical shifts of the backbone (β'-CH_2) and the ring (β-CH_2) protons as well as the vicinal spin-spin coupling between the γ- and β-methylene protons of the ring is responsible for the poor resolution and lack of stereochemical information in the spectrum. This is in contrast to the case of poly(MMA) where high-resolution ^1H NMR has been successfully utilized for the analysis of even pentad sequences.[16] ^{13}C NMR was, however, found to be a more valuable tool for the resolution of configurational sequences in poly(α-MBL). The ^1H-decoupled ^{13}C NMR (67.8 MHz) of a typical, free-radical-polymerized poly(α-MBL) recorded in Me_2SO-d_6 at 100 °C is shown in Figure 4.

The assignment of the peaks was based on the ^1H off-resonance-decoupled ^{13}C spectrum. It may be noted that the backbone quaternary carbon (C_α) appears downfield relative to the backbone CH_2 ($C_{\beta'}$) carbon. In poly(MMA), however, the reverse is known to be the case.[17] The carbonyl carbon at δ 180.2 in poly(α-MBL) showed no stereochemical resolution even at 67.8 MHz, whereas it is known that the carbonyl carbon in poly(MMA) shows pentad resolution even at 20 MHz.[17] The conformational rigidity of the lactone ring in the poly(α-MBL) chain is responsible for the observed lack of resolution of the carbonyl carbon and the methylene carbons in the ring. While a single unresolved carbonyl peak was observed at 20 and 67.8 MHz for poly(α-MBL) prepared by free-radical initiation and with PhMgBr, the corresponding polymer obtained with 9-fluorenyllithium as initiator indicated a doublet structure for the carbonyl carbon, ~0.16 ppm apart. This splitting is unexplained at the moment, except perhaps ascribable to the low DP of the polymer and the possible effect of the 9-fluorenyl end groups. Further work is necessary to examine the nature of the carbonyl carbon resonance in high molecular weight poly(α-MBL) prepared by other possible anionic initiators. The carbonyl and the ring methylene carbons thus provide little stereochemical information.

Fortunately, however, enough rotational flexibility exists, in solution at high temperature, for the chain bonds to permit the stereochemical resolution of the main-chain carbons. In principle, the quaternary carbon (C_α) must show triad resolution and the chain methylene carbon ($C_{\beta'}$) must show diad or tetrad resolution in an atactic polymer. High-resolution ^{13}C NMR (67.8 MHz) in Me_2SO-d_6, indeed, showed the resolution of the quaternary carbon in poly(α-MBL) prepared by free-radical initiation into triads tentatively assigned *rr*, *mr*, and *mm* in the order of increasing field strength (Figure 5), at δ 45.15, 45.3, and 45.58, respectively.

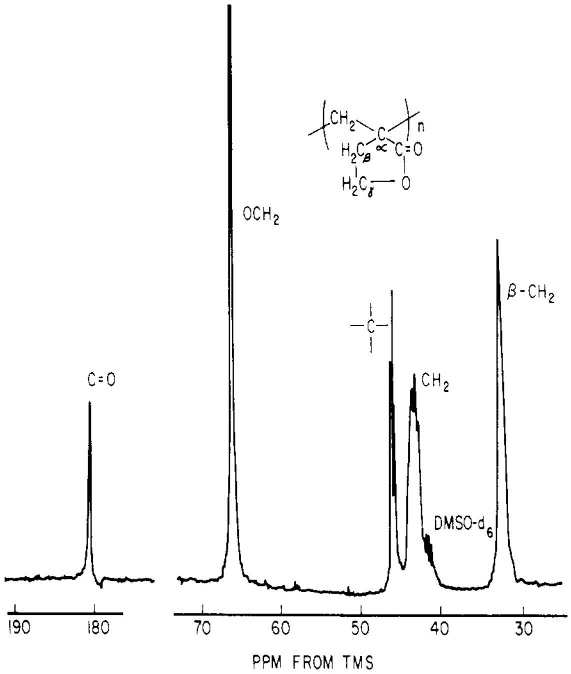


Figure 4. ^1H decoupled ^{13}C NMR spectrum of poly(α-methylene-γ-butyrolactone) polymerized by AIBN at 60 °C (67.8 MHz, in Me_2SO-d_6 at 100 °C).

Since phenylmagnesium bromide in toluene is known to give predominantly isotactic poly(MMA),[14] poly(α-MBL) prepared with this initiator may be assumed to be rich in isotactic sequences. Hence, the large upfield peak in Figure 5B is assigned to the *mm* triad. Thus the present assignment of *rr*, *mr*, and *mm* in the order of increasing field strength for the quaternary carbon in poly(α-MBL) is opposite that of the known assignments for the quaternary carbon in poly(MMA).[17] Poly(α-MBL) prepared by anionic initiation with 9-fluorenyllithium in THF at −78 °C must also be considered rich in isotactic sequences since it shows the predominant upfield peak (Figure 5A). Due to the very small difference in the *mr* and *mm* resonance (0.15 ppm), the latter peak often appeared only as a barely

Table II
Configurational Sequences in Poly(α-methylene-γ-butyrolactone)

	observed[a]			calculated	
polymer type	P_{mm}	P_{mr}	P_{rr}	P_{Σ}	P_m
1. polymer prepared with AIBN, light at 25 °C	0.14	0.46	0.40	0.99	0.37
2. polymer prepared with AIBN at 60 °C	0.14	0.44	0.42	0.95	0.37
3. polymer prepared with t-Bu_2O_2 at 140 °C	0.15	0.45	0.4	0.95	0.38
4. polymer prepared with 9-fluorenyllithium/THF at −78 °C	0.75	0.16	0.09	0.57	
5. polymer prepared with 9-fluorenyllithium/toluene at 0 °C	0.4	0.3	0.3	0.6	
6. polymer prepared with PhMgBr/toluene at −78 °C	0.73	0.17	0.1	0.57	

[a] From the ^{13}C NMR peak areas of the quaternary (C_{α}) carbon; P_m = probability of isotactic diad (m) placement: $P_{\Sigma} = P_{m/r} + P_{r/m}$; $P_{m/r} = P_{mr}/(2P_{mm} + P_{mr})$ and $P_{r/m} = P_{mr}/(2P_{rr} + P_{mr})$. $P_{m/r}$ and $P_{r/m}$ are first-order Markov probabilities, e.g., $P_{m/r}$ is the probability that an m chain end will add a monomer unit syndiotactically (r).

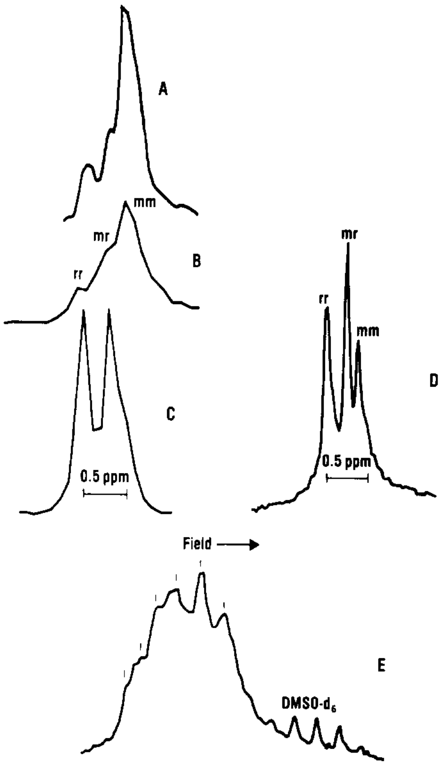


Figure 5. ^{13}C NMR spectrum of the C_{α} region in poly(α-MBL) prepared by (A) 9-fluorenyllithium/THF at −78 °C (20 MHz), (B) C_6H_5MgBr/toluene at −78 °C (20 MHz), (C) AIBN at 60 °C (20 MHz), and (D) AIBN at 60 °C (67.8 MHz); and the (E) C_{β}' region in poly(α-MBL) prepared by AIBN at 60 °C (67.8 MHz).

visible shoulder in the 20-MHz spectrum (Figure 5C) unless spectral parameters are well optimized. In DMF and vinylene carbonate, the *mm* and *mr* peaks could not be resolved. The 67.8-MHz spectrum, however, gave a better resolution (Figure 5D), and even the backbone methylene (C_{β}') at δ 42.6, normally appearing as a broad peak at 20 mHz, appeared to resolve into the six possible tetrads (Figure 5E). In general, however, the quaternary carbon (C_{α}) appears to be the only useful stereochemical probe for determining the tacticity of poly(α-MBL). Triad probabilities estimated from the peak areas for the various types of polymers are shown in Table II.

The triads in polymers from free-radical initiation followed Bernoullian correlation, e.g., $P_{rr} = (1 - P_{mm}{}^{1/2})^2$ or $P_{\Sigma} \simeq 1$ (Table II). The free-radical polymer has a value of $P_m \simeq 0.37$ at 60 °C with very little temperature dependence. This value is, however, higher than the value of $P_m = 0.24$ reported[18] for the free-radical polymerization of MMA indicating that the activation energy difference between the isotactic and syndiotactic propagation is smaller for α-MBL than for MMA. This is consistent with the fact that the steric interaction in the transition state is less than that for α-MBL due to the near planarity of the lactone ring. Such interaction in the isotactic propagation involves only the cyclic methylene units of the growing chain and the approaching monomer unit, while in the case of MMA, it involves the less favorable methyl-methyl interaction. Thus, poly(α-MBL) from free-radical initiation is atactic with slight preponderance of syndiotactic placements although to a much less extent than in poly(MMA). In anionic polymerization, isotactic propagation is favored (Table II) which may be attributed to the preferred geometry of the transition state involving chelation of counterion to the chain end and to the approaching monomer unit.[19] Both 9-fluorenyllithium in THF and phenylmagnesium bromide in toluene gave predominantly isotactic poly(α-MBL) at −78 °C. However, the degree of isotacticity was not high enough to permit crystallization. The polymers were found to be amorphous by X-ray and DSC analysis even after annealing. The triad probabilities of these polymers (Table II) do not follow Bernoullian statistics ($P_{\Sigma} < 1$), but due to lack of information on tetrads, etc., exact correlation with Markov statistics[20] is not possible at this point. It may be noted, however, that even in THF, isotactic propagation is favored for α-MBL in contrast to MMA which is known to give predominantly syndiotactic polymer under these conditions. 9-Fluorenyllithium, in toluene at 0 °C, appears to give block-like polymer with short blocks of *m* and *r* placements, viz., $\bar{N}_m = 3.7$ and $\bar{N}_r = 3$, respectively, where $\bar{N}_m$ = number average length of blocks containing *m* units and vice versa (note: $\bar{N}_m = 1 + 2(P_{mm}/P_{mr})$ and $\bar{N}_r = 1 + 2(P_{rr}/P_{mr})$, ref 20). Experimental conditions leading to predominantly syndiotactic poly(α-MBL) have not yet been determined.

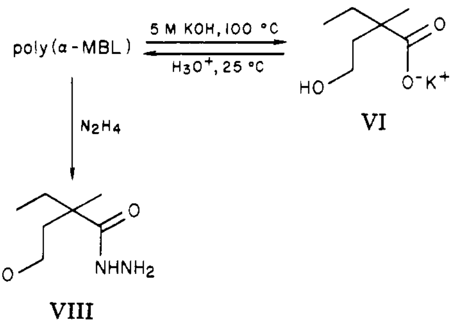
Properties of Poly(α-MBL). The polymer normally obtained by free-radical initiation is atactic and amorphous and has a T_g = 195 °C (by DSC). The polymer is thermally stable to ~320 °C above which it tends to depolymerize. Pyrolysis under vacuum at 350 °C showed α-MBL as the major volatile product. Specimens molded above T_g are clear, hard, and somewhat brittle. Typical properties of polymer (η_{inh} = 1.04) are shown in Table III. Poly(α-MBL) thus seems to resemble poly(MMA) in many of its properties, viz., mechanical properties, clarity, and tendency to depolymerize, etc. Poly(α-MBL), however, has a much higher T_g (195 °C vs. 105 °C for poly(MMA))[21] and considerably better solvent resistance indicating higher structural rigidity of the chain. Unlike poly(MMA) in which the pendant groups have freedom of rotation, poly(α-MBL) has a conformationally rigid lactone ring situated perpendicular to the plane of the backbone, and, hence, in addition to steric restriction, dipole–dipole interactions may also restrict the segmental mobility.

Poly(α-MBL) is not affected by aqueous acids but is

Table III
Some Typical Properties of Poly(α-methylene-γ-butyrolactone) Prepared by Free-Radical Initiation[a]

crystallinity	amorphous
microtacticity	atactic, slightly rich in syndiotactic placements (P_{rr} = 0.43, P_{mr} = 0.44, P_{mm} = 0.13)
T_g, °C	195
thermal stability	major decomposition ⩾320 °C; thermally depolymerizes to monomer
solubility	insoluble in most common organic solvents, soluble in DMF and Me_2SO
tensile strength, psi	9100
ultimate elongation, %	6.5
tensile modulus, psi	2.9 × 10^5

[a] 0.05% AIBN in bulk, η_{inh} = 1.04 (Me_2SO, 25 °C).



slowly hydrolyzed by strong alkali. Treatment with 5 M KOH for several hours at 100 °C gives the highly hydrophilic but water insoluble potassium salt of poly(α-methylene-γ-hydroxybutyric acid) (VI) which showed the characteristic IR band at 1580 cm^{-1} for carboxylate and the absence of lactone carbonyl indicating completion of the saponification. However, the free acid could not be isolated since mere acidification of a suspension of VI in water at 25 °C caused complete lactonization to poly(α-MBL) as indicated by IR (Figures 2C and 2D). The ready tendency of γ-hydroxybutyric acid to form the lactone is well known[22] and appears to be particularly strong in the case of this polymer. Reaction of poly(α-MBL) with hydrazine, a strong nucleophic base, gave water-soluble poly(α-methylene-γ-hydroxybutyric acid hydrazide) (VII).

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Reaction of Phenyllithium with Poly(dichlorophosphazene)[1]

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ABSTRACT: The reaction between poly(dichlorophosphazene), $(NPCl_2)_n$, and phenyllithium has been studied with changes in temperature, reaction time, media, and mole ratio of reactants and in the presence of chelate complexes. The results showed that the chlorine substitution reaction is a slow process, while chain cleavage is much faster and dominates the overall reaction pattern. The nucleophilic replacement of halogen atoms yields high polymers of formula $N_nP_nCl_xPh_y$ that contain up to 10% phenyl-substituent groups. The remaining chlorine atoms can be replaced by treatment with sodium trifluoroethoxide or *n*-butylamine. The properties and molecular structure of the products are discussed.

This work on the synthesis of aryl-substituted polyphosphazenes is an outgrowth of our earlier synthesis of the first high polymeric phosphazenes that contained amino,[2,3] alkoxy, or aryloxy[4] groups. These were formed by the nucleophilic displacement of chlorine in poly(dichlorophosphazene), $(NPCl_2)_n$ (I), by amines, alkoxides, or aryloxides. We now report the reactions of $(NPCl_2)_n$ with phenyllithium with a view to the replacement of chlorine by phenyl to yield polymers with repeating units, such as II or III.

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