# $^{13}$C-NMR Spectroscopy of Poly($\beta$-substituted $\beta$-propiolactone)s. Tacticity Recognition in 1,5-Substituted Polymer System and Stereospecific Contact of Shift Reagent

**Makoto Iida, Shuji Hayase, and Takeo Araki***

*Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan.* *Received July 7, 1977*

ABSTRACT: $^{13}$C-NMR spectroscopy has been found to be effective for observing the dyad tacticity in poly($\beta$-substituted $\beta$-propiolactone)s, a 1,5-substituted polymer system which had been difficult to investigate by $^1$H-NMR spectroscopy. Although the dyad resonances have very similar chemical shifts, $^{13}$C-NMR spectroscopy provides a useful diagnosis for polymer stereoregularity. Addition of a shift reagent, Eu(DPM)$_3$, is helpful for the polymers whose tacticity separation in the $^{13}$C NMR is insufficient. The lanthanide-induced shift occurs stereospecifically, resulting in a stronger low-field shift for meso-dyad signals than for racemic dyad signals. The stereospecificity may be caused by small differences in the pseudocontact angle $\chi_i$ of the Eu ion with the meso- and racemic-dyad units in the polymer chain. In the poly-$\beta$-esters the carbon atoms sensitive to tacticity recognition include the carbonyl carbon and main chain methylene carbon atoms, whereas the methine carbon is insensitive.

Although nuclear magnetic resonance spectroscopy is useful for determination of microtacticity in polymers,[1] the use of this technique has generally been limited to 1,3- and 1,4-substituted polymer systems. In principle, the separation of NMR signals due to chain tacticity depends on the distance between neighboring asymmetric carbon atoms. Based on this principle, a rough guideline of suitability of the NMR technique as a tool for tacticity determination has been discussed[2] for 1,3-, 1,4- and 1,5-substituted polymer systems. In fact, for a series of poly($\beta$-substituted $\beta$-propiolactone)s, i.e., for a 1,5-substituted polymer system, it was shown[2] that the $^1$H-NMR technique (100 MHz) was totally unsuitable for tacticity determination.

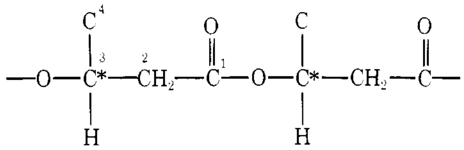
Tacticity determination of poly($\beta$-substituted $\beta$-propiolactone)s has been a key problem encountered in studies of stereoregulation during polymerization. Some poly-$\beta$-esters crystallize without difficulty, even when prepared with a nonstereoregulating catalyst.[3] This characteristic has prevented the presence of crystallinity in these polymers from being used as a criterion of stereoregularity; detailed x-ray crystallography had been the only tool available for distinguishing stereoregular from nonstereoregular polymers.

We previously observed[2] that $^{13}$C-NMR spectroscopy may be more powerful than $^1$H-NMR spectroscopy[4] for characterizing tacticity of some poly-$\beta$-esters. Encouraged by this observation, $^{13}$C-NMR spectra of the polymers were recorded carefully, and dyad tacticities of the poly-$\beta$-esters were measured.

Shift reagents were found to be helpful to improve the separation of dyad signals. The shift reagent Eu(DMP)$_3$ was found to pseudocontact stereospecifically by discriminating meso- and racemic-dyad configurations in the poly-$\beta$-ester chain.

## Results

Poly($\beta$-substituted $\beta$-propiolactone)s may be classified into four types with respect to their $^{13}$C-NMR spectra: (i) Signal splitting due to tacticity is observed without addition of a shift reagent. (ii) Tacticity separation in one of the carbon signals occurs in the absence of a shift reagent, while a shift reagent is required for the other signal to improve the separation. (iii) Tacticity separation is observed only when a shift reagent is added. (iv) No signal splitting due to tacticity is observed in the presence or absence of a shift reagent. The shift reagent used was tris(dipivalomethanato)europium, Eu(DPM)$_3$,[6] added at ca. 25 mol %/mol of polymer repeat groups. $^{13}$C-NMR spectra were recorded in CDCl$_3$ or Me$_2$SO-$d_6$ at 25.16 MHz with a Varian XL-100 spectrometer operating in the F-T mode. The numbering of the carbons in the poly-$\beta$-ester unit is as follows:



$$-O-\underset{H}{\overset{C^{4}}{C^{*}}}{}^{3}-\overset{2}{C}H_2-\overset{O}{\overset{\|}{C}}{}^{1}-O-\underset{H}{\overset{C}{C^{*}}}-CH_2-\overset{O}{\overset{\|}{C}}-$$

**Case i, Poly($\beta$-ethyl $\beta$-propiolactone) (poly(EPL)).** Isotactic poly(EPL) was prepared by polymerization of $\beta$-ethyl $\beta$-propiolactone with (EtAlO)$_n$ catalyst, and the crystalline polymer fraction (poly(EPL)-Al) was purified by extraction with ether. This fraction has been shown[2] to be identical with that obtained using the AlEt$_3$–H$_2$O–epichlorohydrin catalyst,[7] and the latter polymer has been shown to be isotactic by x-ray crystallography.[8] Atactic poly(EPL) was prepared using the Et(ZnO)$_2$ZnEt catalyst. This polymer, which is amorphous, will be designated (poly(EPL)–Zn).

The $^{13}$C-NMR spectra of the isotactic and atactic poly(EPL) samples in CDCl$_3$ (Figure 1), recorded with F-T accumulation under a value of 8192 data points, differ only for the carbonyl carbon ($^1$C) and the methylene carbon ($^2$C) signals. Figure 1A shows the spectrum of isotactic poly(EPL)–Al which was not fully extracted with ether. The $^1$C and $^2$C signals of this sample are composed of intense major singlet signals accompanied by minor signals due to contamination by the nonstereoregular fraction. Repetition of the extraction with ether gave a highly isotactic sample which showed singlet signals for both the $^1$C and $^2$C carbons.

By contrast, the $^1$C and $^2$C carbon signals of atactic poly(EPL)–Zn consist of two signals having nearly identical intensities (Figure 1B). The separation of the $^1$C resonances is 0.12 ppm and that of the $^2$C resonances is 0.15 ppm. The higher field $^1$C signal and the lower field $^2$C signal have the same chemical shift as the corresponding major signals of the poly(EPL)–Al sample. In addition, other $^1$C and $^2$C signals in the poly(EPL)–Zn sample agree well with the minor signals observed in Figure 1A. Thus, the doublets observed for the $^1$C and $^2$C resonances of poly(EPL)–Zn are the result of meso- and racemic-dyad configurations. The assignments of the signals are noted in the figures.

**Case ii, Poly($\beta$-methyl $\beta$-propiolactone) (poly(MPL)).** A comparison of $^{13}$C-NMR spectra of poly(MPL) was made by using three configurationally different samples, i.e., the naturally occurring optically active polymer (designated PHB), isotactic poly(MPL) prepared from a racemic monomer

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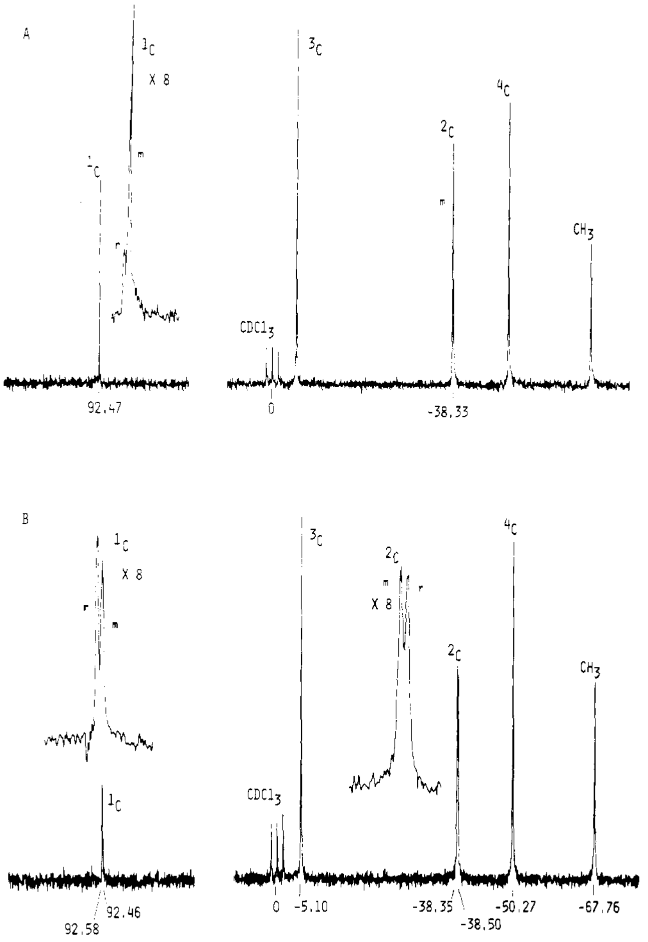

**Figure 1.** $^{13}$C-NMR spectra of poly(EPL) samples in $CDCl_3$. (A) Poly(EPL)–Al (crystalline and isotactic fraction) samples as 10% solution, accumulated with 8000 scans. Fractionated with ether just one time. (B) Poly(EPL)–Zn (amorphous) sample as 8% solution, accumulated with 5000 scans. Sample tubes (12 mm o.d.) were used for measurements. The assignment of the signals was made by off-resonance technique. Accumulations were carried out under a data length value of 8192. The chemical shift values (ppm) are internally standardized from the $CDCl_3$ carbon signal at which the signal-lock was made. The signals of carbonyl carbon and main-chain methylene carbon are expanded (×8) horizontally.

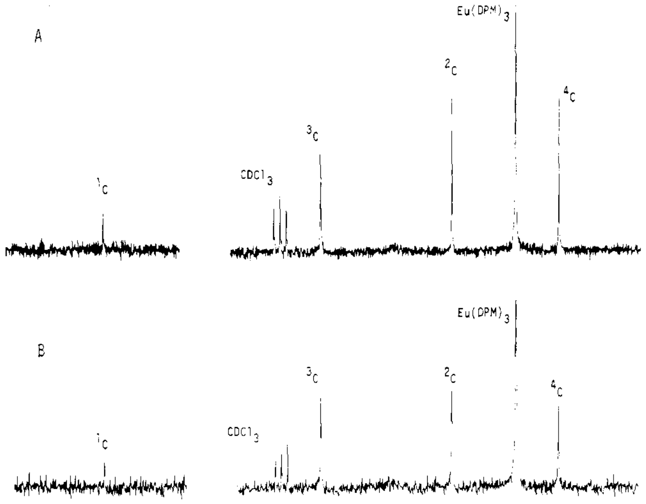

**Figure 2.** $^{13}$C-NMR spectra of isotactic isomers of methyl-substituted poly-β-esters in $CDCl_3$. (A) Naturally occurring PHB sample, an optically active isotactic polymer as 2% solution, accumulated with 8000 scans. (B) Synthetic poly(MPL)–Al sample, an isotactic polymer (acetone-insoluble, crystalline fraction) as 4% solution, accumulated with 5000 scans. In each case 25 mol % of $Eu(DPM)_3$ was added. Other spectroscopic conditions are the same as the case of Figure 1.

mixture using the Al catalyst (designated poly(MPL)–Al), and atactic poly(MPL) prepared using the Zn catalyst (designated poly(MPL)–Zn). The isotactic nature of poly(MPL)–Al has been elucidated previously by x-ray crystallography.[9]

The spectrum of the PHB sample (Figure 2A) and that of the crystalline poly(MPL)–Al sample (Figure 2B) were identical, as would be expected since both samples are isotactic. No splitting of the signals of any of the carbons was observed for these samples in the presence or absence of $Eu(DPM)_3$. In contrast, double $^2$C and $^1$C carbon signals (separation: 0.09 ppm) are observed in spectra of the poly(MPL)–Zn sample under a value of 8192 data points (Figure 3A). When recorded under a lower data-length value of ~4000, no splitting was observed.

Figure 3B shows the spectrum of a 2:1 molar mixture of poly(MPL)–Al and poly(MPL)–Zn. The $^2$C and $^1$C signals consist of pairs of resonances having different intensities, but other carbon signals are observed as singlets. Based on the relative signal intensities of the $^2$C carbon resonances, the lower field signal is due to the meso-dyad configuration and the higher field signal is due to the racemic-dyad configuration. On a similar basis, the lower field $^1$C signal is due to racemic dyads and the higher field signal is due to mesodyad configurations. These assignments are the same as those made in the case of poly(EPL).

Addition of 25 mol % of $Eu(DPM)_3$ (Figure 3C) gives rise to an improved signal separation at the $^2$C resonances (separation: 0.23 ppm), although the signal separation of the $^1$C resonances is reduced. By applying the mixing method described above, the lower field signal of the $^2$C doublet was found to be due to meso-dyad configuration and the higher field signal to racemic-dyad configuration. Thus, the shift reagent contacts more strongly with the meso-dyad unit in the polymer chain than with the racemic-dyad unit, suggesting that the pseudocontact of the Eu ion occurs through discriminating stereochemical environments in the polymer chain.

**Case iii, Poly[β-(2-cyanoethyl) β-propiolactone] (poly(CEPL)).** Crystalline poly(CEPL) was also prepared using the Al catalyst (designated poly(CEPL)–Al), and amorphous polymer was prepared using the Zn catalyst (designated poly(CEPL)–Zn). In the $^{13}$C-NMR spectra of the poly(CEPL)–Zn sample in $Me_2SO\text{-}d_6$ recorded with a data-length value of 8192, two $^1$C carbon resonances were observed (separation: maximum $0.08_7$ ppm) only when a nearly equimolar amount of $Eu(DPM)_3$ was added. Under the same conditions, poly(CEPL)–Al showed a single $^1$C signal, and other carbon spectra were entirely identical with those of poly(CEPL)–Zn. These results indicate that the crystalline poly(CEPL)–Al sample is highly stereoregular and that the amorphous poly(CEPL)–Zn sample contains meso- and racemic-dyad configurations in almost equal proportions.

Preliminary comparison of the $^1$C chemical shift value of the poly(CEPL)–Al sample with those of the poly(CEPL)–Zn indicated that the lower field signal of the latter seems to coincide with the singlet signal of the former. Consequently, if the lanthanide-induced low-field shift occurs more strongly for the meso-dyad configuration than for the racemic-dyad configuration, as observed in the case of poly(MPL), the poly(CEPL)–Al sample must be highly isotactic. The polymerization behavior of the CEPL compound and details of NMR spectroscopy for the polymers will be published elsewhere.

## Discussion

The polymer mixing experiments indicate that the signals of the meso-dyad in the atactic polymers occur at the same

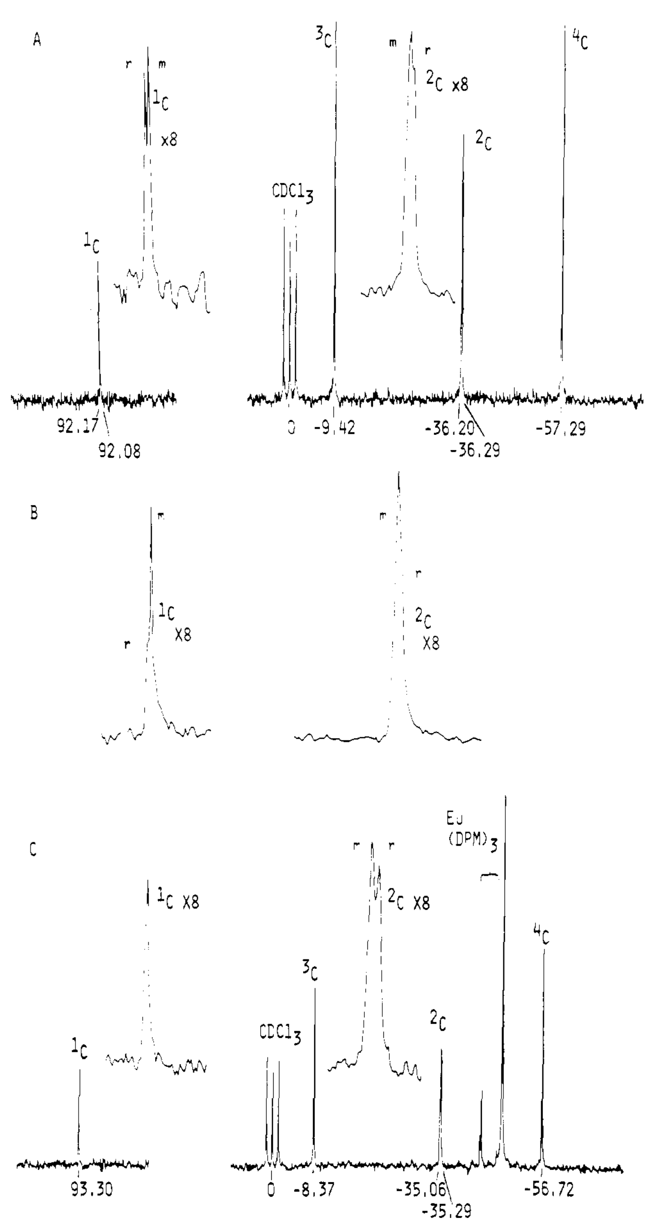

**Figure 3.** $^{13}$C-NMR spectra of amorphous poly(MPL)-Zn sample in CDCl$_3$. (A) In the absence of the shift reagent, 3% solution, and accumulated with 10000 scans. The signals of carbonyl carbon and main-chain methylene carbon are expanded (×8) horizontally. (B) A mixed sample of the poly(MPL)-Zn with the poly(MPL)-Al in a molar ratio of 2:1. Horizontally expanded (×8) signals of the carbonyl carbon and main-chain methylene carbon are shown. No shift reagent was added. The total concentration was 6% accumulated with 3000 scans. (C) Addition of 25 mol % of Eu(DPM)$_3$ to the 3% solution of the poly(MPL)-Zn sample, accumulated with 8000 scans. The signals of the carbonyl carbon and main-chain methylene carbon are expanded (×8) horizontally. Other spectroscopic conditions are identical with the case of Figure 1.

chemical shift as those of the isotactic polymers. This fact clearly shows that differences in the conformations of isotactic and the atactic polymers in solution have a negligible effect on chemical shift. The differences in the $^{13}$C-NMR spectra of the isotactic and the atactic polymers, therefore, can be discussed with respect to the local units of the individual polymers.

For the carbonyl carbon atom in the central position of the 1,5-substituted poly-$\beta$-ester system shown in Figure 4, it can readily be understood that the resonance of this carbon becomes sensitive to dyad configuration (cf. 1 and 2). Since in the absence of the shift reagent the meso-carbonyl carbon signals are observed at a higher field than those of the racemic ones for poly(EPL) and poly(MPL), the meso-carbonyl carbon atom must be subjected to stronger shielding than the racemic-carbonyl carbon atom.

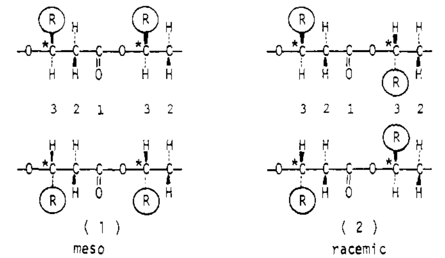

**Figure 4.** Description of meso- and racemic-dyad configurations in the polymer chain. The carbon numbers used in the text are included between the formulas.

The main chain methylene carbon is in close proximity to one of the asymmetric carbons (and simultaneously remote from the other) in the simple dyad formulation. Thus, the resonance of the main chain methylene carbon is also sensitive to dyad configuration, even more so than the carbonyl carbon. The meso-dyad signal of the main chain methylene carbon is observed at a lower field than the corresponding racemic-dyad signal. The racemic-methylene carbon is relatively shielded and the meso-methylene carbon is relatively deshielded, in reverse to the case of the carbonyl carbon atom. Examination of space-filling models shows that when every bond except for CO–O rotates freely, no specific shielding effect is expected for $^1$C and $^2$C carbons in stereochemically different dyad units in the 1,5-substituted system. Hindered rotation about the $^1$C–$^2$C bond seems to be a requirement for such shielding effects as are observed for meso and racemic dyads.

It is important that the tacticity separation of the signals takes place only for the $^1$C and $^2$C atoms which are subjected to larger induced shifts by contact of the Eu(DPM)$_3$ molecule. Namely, the net downfield shifts induced by Eu(DPM)$_3$[10] were observed for poly(MPL) as follows: $^1$C, av 1.18; $^2$C, av. 1.14; $^3$C, av 1.05, and $^4$C, av 0.57 ppm. This fact indicates that the O=$^1$C and $^2$C are more readily accessible to the shift reagent (or solvent molecules)[11] than $^3$C and $^4$C. Stereospecific pseudocontact of the Eu ion is likely to arise from differences in the contact angles of the Eu ion toward neighbors of O=$^1$C and $^2$C of the meso- and racemic-dyad units.

Calculation of the contact angles ($\chi_i$) was made from the observed shift values ($\Delta\delta_i$) by using the equation[12,13] $\Delta\delta_i = k(3\cos^2\chi_i - 1)/R_i^{\,3}$ and by taking into account that the Eu ion contact occurs with the same distance ($R_i$) toward meso- and racemic-dyad units. The difference in the $\chi_i$ for the two dyad units ($\Delta\chi_i$) amounts to 1–4°, depending on the standard contact angles taken arbitrarily.[14] Although this value is small, examination of space-filling models for the meso- and racemic-dyad units indicates that this difference in the contact angle becomes reasonable when rotation about the $^1$C–$^2$C bond is hindered. Otherwise, no reason for stereospecific pseudocontact of the Eu ion can be found because the 1,5-substituted meso-and racemic-dyad units take very similar conformations by rotating quite arbitrarily.

## Experimental Section

**Materials.** Poly($\beta$-hydroxybutyrate) (PHB) was provided by Professor S. Fukui's laboratory, Kyoto University. Isotactic poly($\beta$-methyl $\beta$-propiolactone) (poly(MPL)) and isotactic poly($\beta$-ethyl $\beta$-propiolactone) (poly(EPL)) were prepared with the (EtAlO)$_n$ catalyst and fractionated, according to the methods previously described.[2] Atactic poly(MPL) and poly(EPL) samples were prepared with the Et(ZnO)$_2$ZnEt catalyst and were purified according to the methods previously described.[2]

Crystalline and amorphous poly[$\beta$-(2-cyanoethyl) $\beta$-propiolactone] (poly(CEPL)) samples were prepared by ring-opening polymerization of the corresponding monomer with the $(EtAlO)_n$ and $Et(ZnO)_2ZnEt$ catalysts, respectively, and were fractionated with acetone.[15]

**$^{13}$C-NMR Spectroscopy.** $^{13}$C-NMR spectra were recorded at 38°C with a Varian Model XL-100 spectrometer at 25.16 MHz with an F-T accumulator. The number of data points utilized for the F-T accumulation was 8192. For the poly(MPL), PHB, and poly(EPL) samples, the spectra were taken in $CDCl_3$ solution, and for the poly(CEPL) samples the data were taken in $Me_2SO$-$d_6$ solutions. The chemical shift values noted in Figures 1–3 were internally standardized from the solvent signals. The errors in the chemical shift values were ±0.04 ppm when the $Eu(DPM)_3$ reagent was absent and ±0.2 ppm when the shift reagent was present. The separation between meso-dyad and racemic-dyad signals was ±0.04 ppm for the $^1$C signals, ±0.07 ppm for the $^2$C signals in the absence of the shift reagent, and ±0.1 ppm for the $^2$C signals of the poly(MPL) in the presence of the shift reagent. The $\Delta\delta$ values used for describing the induced shift by the shift reagent is in the accuracy of ±0.2 ppm.

The $Eu(DPM)_3$ shift reagent was found to give the best results among the shift reagents tested. The optimum concentration of the $Eu(DPM)_3$ reagent was predetermined so as to minimize line broadening and insolubilization and to maximize the signal separation. The mol % concentration was defined as $Eu(DPM)_3$ mol % of mol monomer unit in the polymers.

**Acknowledgments.** The authors express their thanks to Dr. K. Lee of our Department for recording $^{13}$C-NMR spectra and for helpful discussions. A gift of the PHB sample from Professor Saburo Fukui's laboratory of Kyoto University and encouragement by the late Professor H. Tani are gratefully acknowledged.

## References and Notes

(1) F. A. Bovey, "High Resolution NMR of Macromolecules", Academic Press, New York, N.Y., 1972.

(2) M. Iida, T. Araki, K. Teranishi, and H. Tani, *Macromolecules*, **10,** 275 (1977).

(3) (a) R. Thiebout, N. Fisher, Y. Etienne, and I. Coste, *Ind. Plast. Mod. Elastomeres*, **14,** 1 (1962); (b) J. Cornibert, R. H. Marchessault, A. E. Allegrezza, Jr., and R. W. Lenz, *Macromolecules*, **6,** 676 (1973).

(4) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 452; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance For Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 149; (c) M. W. Duch and D. M. Grant, *Macromolecules*, **3,** 165 (1970).

(5) J. Delsarte and G. Weill, *Macromolecules*, **7,** 343 (1974).

(6) R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents", Academic Press, New York, N.Y., 1973; R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11,** 675 (1972).

(7) K. Teranishi, M. Iida, T. Araki, S. Yamashita, and H. Tani, *Macromolecules*, **7,** 421 (1974).

(8) M. Yokouchi, Y. Chatani, H. Tadokoro, and H. Tani, *Polym. J.*, **6,** 248 (1974).

(9) M. Yokouchi, Y. Chatani, H. Tadokoro, K. Teranishi, and H. Tani, *Polymer*, **14,** 267 (1973).

(10) The direction of the shift is normal for Eu ion and is consistent with the case of proton shift in PHB induced by $Eu(fod)_3$ and $Eu(thd)_3$ (ref 5).

(11) The polymer structure in solution would be highly sensitive to the solvent used. The fact that the tacticity separation of the poly(CEPL) samples was observed only at high concentration of the shift reagent may be due to high polarity of $Me_2SO$. For the poly(EPL) sample, benzene was a poor solvent for tacticity separation.

(12) For simplification, the pseudocontact mechanism is considered predominant here, and contact or direct interaction mechanisms are neglected. Validity of the pseudocontact approximation in the $^{13}$C NMR has been extensively discussed in ref 13. For the pseudocontact approximation, good correlations between $^1$H- and $^{13}$C-lanthanide shifts are shown in ref 13, though minor deviations due to contact mechanism were observed for the $^{13}$C case.

(13) G. E. Hawkes, C. Marzin, D. Leibfritz, S. R. Johns, K. Herwig, R. A. Cooper, D. W. Roberts, and J. D. Roberts ref 6, p 129.

(14) This value was estimated from the shift values at a concentration of the shift reagent of 25 mol % to polymer unit, and the standard $\chi_i$ value for the racemic- or meso-dyad unit is not determined. The smaller $\Delta\chi_i$ value (~1°) was determined by assuming the $\chi_i \sim 0°$ or $\sim 180°$. More probable $\Delta\chi_i$ values will be in a range of 2–4°.

(15) T. Araki, S. Hayase, and M. Iida, unpublished results.

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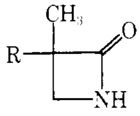
# Polymerization of $\alpha,\alpha$-Disubstituted $\beta$-Propiolactones and Lactams. 14. Substituent, Solvent, and Counterion Effects in the Anionic Polymerization of Lactones

**Ebrahim Bigdeli**[†] **and Robert W. Lenz***

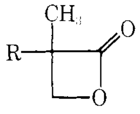
*Materials Research Laboratory, Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003.* *Received November 23, 1978*

ABSTRACT: A series of $\beta$-propiolactones, substituted in the $\alpha$ position by two alkyl groups, was polymerized in two different dipolar aprotic solvents with two different anionic initiators. The anionic, ring-opening, polymerization reactions involved are bimolecular nucleophilic substitutions which show an apparent steric acceleration, but the increase in propagation rate constants observed with increasing size of the $\alpha$ substituent can be rationalized on the basis of either steric inhibition to ion-pair formation or a favorable hydrophobic interaction. The solvent effects observed are attributed to a greater importance of anion solvation than cation solvation in these ion pair reactions.

Previous publications from this laboratory have described the unusual substituent effects on the rates of anionic, ring-opening, polymerization reactions in dimethyl sulfoxide ($Me_2SO$) for a series of $\beta$-propiolactams which were substituted in the $\alpha$ position with two alkyl groups, Ia–d, as follows.[1]



Ia, R = $CH_3$
b, R = $CH_2CH_3$
c, R = $(CH_2)_2CH_3$
d, R = $(CH_2)_3CH_3$



IIa, R = $CH_3$
b, R = $CH_2CH_3$
c, R = $(CH_2)_2CH_3$
d, R = $(CH_2)_3CH_3$

It was observed that when one of the substituents was the methyl group and the other was systematically increased in size within the $n$-alkyl homologous series as shown above, the apparent propagation rate constants unexpectedly increased with increasing size of the alkyl group.

Two possible explanations were offered for this reverse steric effect;[2] these were: (1) the larger alkyl group in the ultimate unit of the active polymer chain increasingly interferes with the approach of the cation to the carboxylate anion end group thereby increasing the reactivity of the carboxylate nucleophile by imparting more free-ion character to the end group ion pair, or (2) the larger alkyl groups in the polymer

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[†] Department of Chemistry, University for Teacher Education, Tehran, Iran.