with $r_H/r_C \geqslant 1.4$. This is a significant observation, since we are currently unable to investigate sequence distribution by NMR methods. The conclusion that the polymer is at least close to having a completely random structure is interesting in view of the fact that the monomers probably have different reactivities and that TPA is insoluble in the initial synthesis mixture. It seems likely that transesterification will randomize the copolymer at a relatively early stage of the synthesis, perhaps after the formation of oligomers.

Acknowledgment. This research was supported by NSF Grant No. DMR84-17525 and by Dartco Manufacturing Inc. We are indebted to Dr. N. D. Field and his colleagues at Dartco, Augusta, GA, for synthesizing and processing the specimens of the copolymer in the form of as-spun and annealed fibers and also molded plaques.

Registry No. (HBA)(TPA)(BP) (copolymer), 31072-56-7.

References and Notes

(1) Wood, A. S. *Mod. Plast.* **1985**, April, 78.
(2) "Plastiscope", *Mod. Plast.* **1984**, Dec, 14.
(3) Gutierrez, G. A.; Chivers, R. A.; Blackwell, J.; Stamatoff, J. B.; Yoon, H. *Polymer* **1983**, *24*, 937.
(4) Blackwell, J.; Biswas, A. *Macromolecules* **1985**, *18*, 2126.
(5) Blackwell, J.; Biswas, A. *Macromol. Chem.—Macromol. Symp.* **1986**, *2*, 21.
(6) Blackwell, J.; Cageao, R. A.; Biswas, A. *Macromolecules*, in press.
(7) Mitchel, G. R.; Windle, A. H. *Colloid Polym. Sci.* **1985**, *263*, 230.
(8) Blackwell, J.; Gutierrez, G. A.; Chivers, R. A.; Ruland, W. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22* 1343.
(9) Bonart, R. C.; Blackwell, J.; Biswas, A. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 353.
(10) Field, N. D. *Polym. Process. Soc.* **1986**, Montreal, April.
(11) Biswas, A.; Blackwell, J., manuscript in preparation.

Side-Chain Effects on Ultraviolet Absorption of Organopolysilane Radical Anions

Hiroshi Ban* and Ken Sukegawa

NTT Electrical Communications Laboratories, Tokai Ibaraki 319-11, Japan

Seiichi Tagawa

Research Center for Nuclear Science and Technology, University of Tokyo, Tokai Ibaraki 319-11, Japan. *Received June 2, 1987*

ABSTRACT: Eight kinds of organopolysilane radical anions in tetrahydrofuran solution were investigated utilizing the pulse radiolysis technique. UV absorption maxima of poly(alkylsilane) radical anions are observed at 355–363 nm. Introducing a methylphenylsilylene unit or diphenylsilylene unit into the polymer chains causes a slight red shift in the UV absorption of their radical anions. This can be understood on the basis of an electronic interaction between the silicon main chain and pendant phenyl groups. Extinction coefficients of these radical anions were determined to be 1.4–2.1 × 10^5 per mol of added electron.

Introduction

In our previous report, high molecular weight organopolysilane radical anions were first observed by utilizing the pulse radiolysis technique with 2-ns time resolution.[1] Poly(methylpropylsilane) (PMPrS) and poly(methylphenylsilane) (PMPS) radical anions in tetrahydrofuran (THF) solutions were investigated, and their optical properties and kinetics were discussed. On the other hand, cyclic organopolysilane radical anions such as $(Si(CH_3)_2)_n$ (n = 4–6) and $(Si(C_6H_5)_2)_m$ (m = 4, 5) have been already observed by reduction with alkali metal.[2-5] ESR studies have shown that unpaired electrons of these cyclic radical anions are delocalized over the ring skeleton.[3,5] Added electrons of PMPrS and PMPS radical anions are also considered to delocalize along the catenating silicon chain.

Organopolysilane solid films reveal high electric resistance but become p-type semiconductors in the presence of strong electron acceptors such as AsF_5 or SbF_5.[6] This may suggest that catenating silicon atoms of organopolysilane molecules can be essentially a semiconducting path. Ionic or charge-transfer states are often related to electric properties. Study of polysilane radical anions is of interest from the viewpoint of the potential semiconductivity of the silicon chain. The pulse radiolysis technique is very useful in that the dynamic behavior of polysilane radical anions can be observed.

Organopolysilanes have strong absorption bands in the 300–360-nm region. Absorption peaks (λ_{max}) of poly(alkylsilanes) are usually found at 300–320 nm, which have been attributed to a transition from the highest occupied silicon σ orbital to the σ^* orbital.[7] However, λ_{max}'s of poly(arylsilanes) such as PMPS or diphenylsilane copolymers occur at 340–360 nm.[8] This red shift indicates the contribution of π–σ^* character for the transition according to the aryl substituents.[7,9,10] Similar electronic interaction between the silicon main chain and aryl substituents can be anticipated for polysilane radical anions. In this report, eight other kinds of polysilane radical anion in THF solutions are investigated by pulse radiolysis, and side-chain effects on their optical properties are discussed.

Experimental Section

The following polymers were synthesized according to the conventional method:[11-13] poly(β-phenethylmethylsilane) (PPnMS); poly[(dimethylsilane)-*co*-(methylcyclohexylsilane)] (DMS–MHxS); poly[(dimethylsilane)-*co*-(methylpropylsilane)] (DMS–MPrS); poly[(dimethylsilane)-*co*-(β-phenethylmethylsilane)] (DMS–PnMS); poly[(dimethylsilane)-*co*-(methylphenylsilane)] (DMS–MPS); poly[(diphenylsilane)-*co*-(dimethylsilane)] (DPS–DMS); poly[(diphenylsilane)-*co*-(methylpropylsilane)] (DPS–MPrS); poly[(diphenylsilane)-*co*-(β-phenethylmethylsilane)] (DPS–PnMS). Molar monomer feed ratios of these copolymers were fixed to 1:1. Molecular weights were determined by gel permeation chromatography (GPC). Compositions of these copolymers were determined by ^1H NMR signal intensities, except DMS–MHxS and DMS–MPrS, whose compositions were determined by ^{13}C NMR. Their compositions and molecular weights are listed in Table I.

0024-9297/88/2221-0045$01.50/0

Table I
Molecular Weights and Compositions of Polysilanes

polymer	composition[a]	$M_w \times 10^{-3}$	M_w/M_n	R[b]
PPnMS	$(MePhenSi)_n$	702	1.9	
DMS-MHxS	$(Me_2Si)_{0.4}(Me\text{-}c\text{-}HexSi)_{0.6}$	665, 13	2.5, 2.3	0.62
DMS-MPrS	$(Me_2Si)_{0.3}(MePrSi)_{0.7}$	985, 11	2.2, 1.8	0.19
DMS-PnMS	$(Me_2Si)_{0.4}(MePhenSi)_{0.6}$	279, 10	1.7, 1.9	0.27
DMS-MPS	$(Me_2Si)_{0.4}(MePhSi)_{0.6}$	1080, 8	2.9, 2.1	0.77
DPS-DMS	$(Ph_2Si)_{0.5}(Me_2Si)_{0.5}$	471, 3	1.9, 1.8	0.19
DPS-MPrS	$(Ph_2Si)_{0.5}(MePrSi)_{0.5}$	1010, 4	3.2, 2.1	0.71
DPS-PnMS	$(Ph_2Si)_{0.5}(MePhenSi)_{0.5}$	719	4.2	

[a] Phen = phenethyl; Me = methyl; c-Hex = cyclohexyl; Pr = propyl; Ph = phenyl. [b] R is the ratio of the high molecular weight fraction of the bimodal distribution to the low molecular weight fraction from the GPC elution profile.

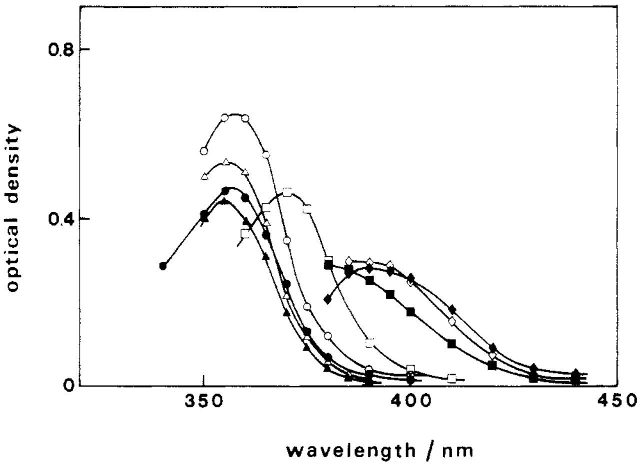

Figure 1. Transient UV absorption spectra of organopolysilanes at 40 ns after an electron pulse; cell length = 1 cm: (○) PPnMS; (●) DMS-MHxS; (△) DMS-MPrS; (▲) DMS-PnMS; (□) DMS-MPS; (■) DPS-DMS; (◇) DPS-MPrS; (◆) DPS-PnMS. Abbreviated forms are referred to in Table I.

Pulse radiolysis measurement was performed by using the linear accelerator instruments at the University of Tokyo.[14-16] Polymer solutions in THF were irradiated by a 35-MeV single-pulse electron beam at room temperature, and their ultraviolet-visible (UV-vis) absorption spectra were recorded. The pulse width was 2 ns and the acquisition time was 200 or 500 ns with the ordinal investigation in nanosecond time region. A new pulse radiolysis system[16] was also employed for the observation of the primary process in the picosecond time region. All sample solutions were prepared on the vacuum line. THF was dehydrated with sodium metal and distilled into the cell on the line. The samples were degassed 3 times under 2×10^{-4} Torr. Polymer concentrations were usually more than 100 mM (average Si unit).

Results and Discussions

Transient absorption spectra of the polymer solutions in THF in 40 ns after an electron pulse are shown in Figure 1. These are difference spectra before and after pulse irradiation and therefore represent the newly produced species, polysilane radical anions. Polysilane radical anions are produced by reaction with the solvated electron generated by electron pulse irradiation. Shorter wavelength regions from ca. 20 nm and below are too opaque due to strong polymer absorption.

The λ_{max}'s of DMS-MHxS and DMS-MPrS radical anions were both at 356 nm. This is close to the previously reported λ_{max} value of the PMPrS radical anion.[1] λ_{max}'s of polysilanes containing phenyl-substituted alkyl groups such as PPnMS and DMS-PnMS appeared in the same position, 357 and 355 nm, respectively. This indicates that electronic states of polysilane radical anions are not perturbed if the first segment directly attached to the silicon atom is an alkyl group, without regard to the existence of phenyl groups at a more distant position. It was also observed that λ_{max}'s of PPnMS and DMS-PnMS lie at 305 and 303 nm, respectively, indicating no electronic interaction between phenyl groups of phenethyl substituents in the neutral state.

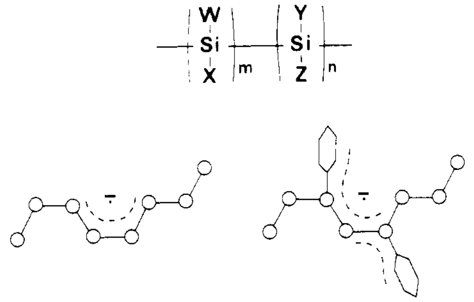

Figure 2. Schematic structure of organopolysilane radical anions. W, X, Y, and Z substituents in the molecular structure represent alkyl or aryl groups. Poly(alkylsilane) radical anion is described on the left side by using a simple skeletal model where alkyl groups are omitted. Extra charge is dispersed along the silicon main chain. Poly(arylsilane) radical anion is in the right side, and extra charge is dispersed on the phenyl groups as well as the main chain.

The λ_{max} of the DMS-MPS radical anion appears at 370 nm, close to the 372-nm value for the PMPS radical anion. This 370–372-nm value is somewhat longer than the λ_{max}'s of poly(alkylsilane) radical anions discussed above. The λ_{max} of the DPS-PnMS radical anion was 390 nm, which was still longer than λ_{max}'s of DMS-MPS and PMPS radical anions. Regarding DPS-DMS and DPS-MPrS radical anions, λ_{max} regions were opaque due to the polymer absorption and only the tailing curves were measurable. The λ_{max}'s of DPS-DMS and DPS-MPrS radical anions were estimated to lie at ca. 380 and ca. 385 nm, respectively, judging from their tailing curves.

The λ_{max}'s of poly(alkylsilanes), polysilanes containing a methylphenylsilylene unit, and polysilanes containing a diphenylsilylene unit appeared at 355–363, 370–372, and 380–390 nm, respectively. λ_{max}'s of polysilane radical anions were found to show a red shift due to pendant groups, similar to what is observed for polysilane absorption. This red shift from 355 to 390 nm is thought to arise from electronic interaction between the silicon main chain and phenyl groups directly attached to silicon atoms. MO calculation on organopolysilanes showed that the Si_{3p} band of the main chain and the C_{2p} band of the phenyl groups may undergo σ-π mixing.[7] Photoelectron spectroscopic analysis also indicates the same admixture.[9] Similar electronic interaction may exist in polysilane radical anions. The added electron is thought to delocalize over phenyl groups as well as the silicon main chain. The schematic structure of polysilane radical anions is shown in Figure 2.

A typical rise of UV absorption after an electron pulse irradiation is shown in Figure 3. Optical density of PMPrS radical anion was monitored at 360 nm. The

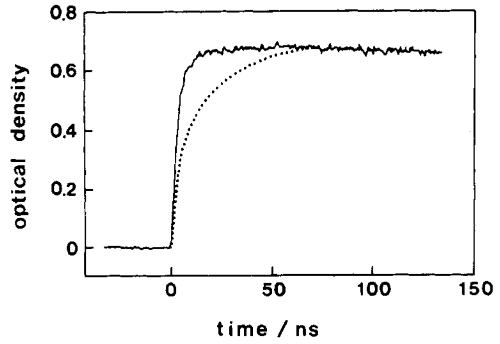

Figure 3. Rise of UV absorption of the poly(methylpropylsilane) radical anion in the nanosecond time region, monitored at 360 nm. Polymer concentration was 93 (solid line) and 12 mM (dotted line); cell length = 1 cm.

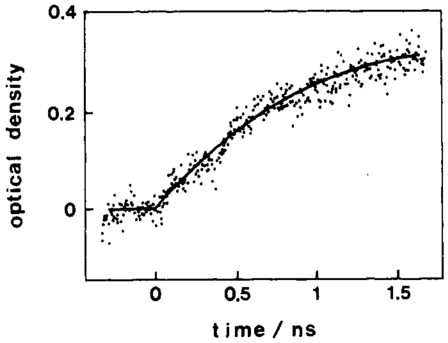

Figure 4. Rise of UV absorption of the poly(methylpropylsilane) radical anion in the picosecond time region, monitored at 375 nm. Polymer concentration was 200 mM; cell length = 2 cm.

growth of the absorption observed for the 93 mM solution reached a maximum value in ca. 20 ns and did not decay in an acquisition time. For 12 mM solution, the growth was complete in ca. 70 ns. Growth of other polysilane radical anions consisting of alkylsilylene units and/or a methylphenylsilylene unit was similarly complete within ca. 20 ns when polymer concentrations were higher than 100 mM. All radical species were quite stable and did not decay within 500 ns.

The rise in the picosecond time region with the resolution of 20 ps was observed by utlizing a new picosecond pulse radiolysis system.[16] PMPrS solution in THF was investigated at 375 nm. The 360–370-nm region was somewhat opaque due to high polymer concentration (200 mM) and long cell length (2 cm). Optical density at 375 nm was increased monotonously after a single electron pulse irradiation as shown in Figure 4. This figure represents the electron transfer reaction in the picosecond time region. Following the reaction in nanosecond time region corresponds to Figure 3. Only the generation of PMPrS radical anion was observed in the picosecond time regions.

Extinction coefficients (ϵ) of the radical anions were measured by using pyrene as an electron scavenger. λ_{max} of pyrene radical anion is 495 nm and its extinction coefficient is 49 500 M^{-1} cm^{-1}.[17] Kinetic treatment of the electron-transfer reaction from polysilane radical anions to pyrene can give ϵ values of the polymer radical anions. Details of the reactions and treatments were described in the previous paper.[1] The ϵ and λ_{max} values obtained are summarized in Table II together with PMPrS and PMPS data. All ϵ values were quite large, 1.4–2.1 × 10^5 per mol of added electron (including 10–20% for experimental error). These large extinction coefficients may possibly be attributed to the fact that the extra charge on the polymer chain is very polarizable.

Table II
Absorption Maxima (λ_{max}) and Extinction Coefficients (ϵ)[a] of Organopolysilanes and Their Radical Anions

	polymers		radical anions	
	λ_{max}, nm	$\epsilon \times 10^{-3}$, M^{-1} cm^{-1}	λ_{max}, nm	$\epsilon \times 10^{-5}$, M^{-1} cm^{-1}
PMPrS[b]	306	5.9	363	1.6
PPnMS	305	6.6	357	2.1
DMS–MHxS	305	6.5	356	1.8
DMS–MPrS	302	5.2	356	1.6
DMS–PnMS	303	6.8	355	1.5
DMS–MPS	331	7.0	370	1.6
PMPS[b]	340	11.0	372	1.6
DPS–DMS	340	5.0	ca. 380	1.4
DPS–MPrS	352	6.0	ca. 385	1.4
DPS–PnMS	356	8.4	390	1.4

[a] Extinction coefficients are defined as per average Si unit for polymers and per added electron for radical anions. [b] Reference 1.

The concentration of polysilane radical anions was calculated from optical densities and absorption coefficients to be ca. 2.5 × 10^{-6} M. Sample concentrations were so high that a single polymer chain can receive only one excess electron. Therefore, only one radical anion structure such as is shown in Figure 2 may exist in each polymer chain. This feature reminds us of the postulated behavior of a polaron.[18]

Conclusion

Eight kinds of organopolysilane radical anions were investigated by means of pulse radiolysis with 2-ns time resolution. The radical anions were quite stable in THF solution. Radical anions of poly(alkylsilanes) such as PMPrS, DMS–MPrS, and DMS–MHxS exhibited λ_{max}'s at 355–363 nm. Those of PPnMS and DMS–PnMS showed almost the same λ_{max}. The phenethyl group behaves like an alkyl group. λ_{max}'s of DMS–MPS and PMPS radical anions were 370–372 nm, and those of DPS–DMS, DPS–MPrS, and DPS–PnMS radical anions were at still longer wavelengths, 380–390 nm. This red shift can be understood on the basis of an electronic interaction between silicon main chain and phenyl groups. Extinction coefficients of these radical anions were determined to be 1.4–2.1 × 10^5 M^{-1} cm^{-1}.

Acknowledgment. We express our appreciate to N. Hayashi of the University of Tokyo for his experimental help.

Registry No. PPnMS (homopolymer, radical anion), 88002-80-6; (DMS)(MHXS) (copolymer), 88993-02-6; (DMS)(MPrS) (copolymer), 71092-17-6; (DMS)(PnMS) (copolymer, radical anion), 88993-05-9; (DMS)(MPS) (copolymer, radical anion), 70158-17-7; (DPS)(DMS) (copolymer, radical anion), 70926-75-9; (DPS)(MPrS) (copolymer, radical anion), 111409-87-1; (DPS)(PnMS) (copolymer, radical anion), 99635-05-9.

References and Notes

(1) Ban, H.; Sukegawa, K.; Tagawa, S. *Macromolecules* **1987**, *20*, 1775.
(2) West, R.; Carberry, E. *Science (Washington, D.C.)* **1975**, *189*, 179.
(3) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.
(4) Kira, M.; Bock, H.; Hengge, E. *J. Organomet. Chem.* **1979**, *164*, 277.
(5) West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1983; Vol. 9, pp 365–397.
(6) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. *J. Am. Chem. Soc.*, **1981**, *102*, 7352.
(7) Takeda, K.; Teramae, H.; Matsumoto, N. *J. Am. Chem. Soc.* **1986**, *108*, 8186.
(8) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.

(9) Loubriel, G.; Zeigler, J. *Phys. Rev. B* **1986**, *33*, 4203.
(10) Pitt, C. G.; Carey, R. N.; Toren, E. C., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3806.
(11) Trefonas, P., III; Djurovich, P. I.; Zhang, X.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819.
(12) Zhang, X.; West, R. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 159.
(13) Zhang, X.; West, R. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *23*, 479.
(14) Kobayashi, H.; Ueda, T.; Kobayashi, T.; Tagawa, S.; Tabata, Y. *Nucl. Instrum. Methods* **1981**, *179*, 223.
(15) Kobayashi, H.; Ueda, T.; Kobayashi, T.; Washio, M.; Tagawa, S.; Tabata, Y. *Radiat. Phys. Chem.* **1983**, *21*, 13.
(16) Tabata, Y.; Kobayashi, H.; Washio, M.; Yoshida, Y.; Hayashi, N.; Tagawa, S. *J. Radioanal. Nucl. Chem.* **1986**, *101*, 163.
(17) Gill, D.; Jagur-Grodzinsky, J.; Swarc, M. *Trans. Faraday Soc.* **1964**, *60*, 1424.
(18) Rice M. J.; Phillpot, S. R. *Phys. Rev. Lett.* **1987**, *58*, 937.

Conformation and Dynamic Aspects of Poly(γ-*n*-octadecyl L-glutamate) in the Solid State and Liquid-Crystalline State As Studied by Variable-Temperature ^{13}C CP/MAS NMR Spectroscopy

Takeshi Yamanobe,† Makoto Tsukahara,† Tadashi Komoto,† Junji Watanabe,† Isao Ando,*† Ichitaro Uematsu,‡ Kenzo Deguchi,§ Teruaki Fujito,§ and Mamoru Imanari§

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan, Department of Clothing, Tokyo Kasei University, Kaga, Itabashi-ku, Tokyo, Japan, and JEOL Ltd., Nakagami, Akishima, Tokyo, Japan. *Received April 16, 1987*

ABSTRACT: ^{13}C CP/MAS NMR experiments are carried out for poly(γ-*n*-octadecyl L-glutamate) as a function of temperature, in order to elucidate dynamic and conformational features in the solid state and liquid-crystalline state. From these experimental results, it is found that the main chain of the polymer takes on a right-handed α-helical conformation within the temperature range from 27 to 100 °C, while long *n*-alkyl side chains take on an all-trans zigzag conformation in the crystalline state at room temperature and are in a mobile state above 35 °C. Further, it is found that at about 40 °C the α-helical main chain in the liquid-crystalline phase is undergoing molecular motion at a frequency of ca. 60 kHz.

Introduction

Recently, Watanabe et al.[1] have reported that in a series of α-helical poly(L-glutamates) with *n*-alkyl side chains of various lengths (*n* (number of carbon atoms in the alkyl group) = 4–18), *n*-alkyl side chains longer than *n* = 10 form a crystalline phase composed of paraffin-like crystallites together with the α-helical main chain packing into a characteristic layer structure. The polymers form thermotropic cholesteric liquid crystals by the melting of the side-chain crystallites. In order to investigate the structure and dynamics of these thermotropic cholesteric liquid crystals, it is important to collect detailed information about the main-chain and side-chain structures and motions at various temperatures.

It has been demonstrated that ^{13}C cross polarization/magic angle spinning (CP/MAS) spectroscopy is a very powerful tool for structural analysis of polymers in the solid state.[2] In a previous paper,[3] it was reported that, from the observation of ^{13}C NMR chemical shifts in the solid state, the main chain of poly(γ-*n*-alkyl L-glutamate) assumes a right-handed α-helical conformation irrespective of side chain length and that in the side-chain crystallites the *n*-alkyl chain assumes an all-trans zigzag conformation.[3] In these studies, ^{13}C CP/MAS experiments have been carried out only at room temperature. If ^{13}C CP/MAS NMR experiments can be done as a function of temperature, such experiments may present the potential for detailed insight into the molecular structure and dynamics of these polymers in the solid state and liquid-crystalline state.

The purpose of this work is to investigate the structure and dynamics of poly(γ-*n*-octadecyl L-glutamate) with a long *n*-alkyl chain in the solid state and liquid-crystalline state as a function of temperature.

Experimental Section

Materials: Poly(γ-*n*-octadecyl L-glutamate) (PG-18, where the number of carbon atoms in the *n*-alkyl group follows the letters PG) was synthesized by ester-exchange reactions between poly(γ-methyl L-glutamate) (M_v = 100 000) and *n*-octadecyl alcohol as described in a previous paper.[1] The complete replacement of methyl groups by *n*-alkyl groups was confirmed by the ^{1}H NMR spectra. The film of PG-18 was prepared by casting the solution from chloroform at room temperature.

Measurements. ^{13}C CP/MAS NMR spectra were measured by means of JNM-GX270 NMR (67.5 MHz) with a variable-temperature (VT) CP/MAS accessory at temperatures from room temperature (27 °C) to 100 °C. The sample (ca. 200 mg) was contained in a cylindrical rotor made of ceramic materials and spun at 4.5–4.8 kHz. Contact time is 2 ms and repetition time 5 s. Spectral width and data points were 27 kHz and 8K, respectively. ^{1}H field strength was 1.6 mT for both the CP and decoupling process. The number of accumulations was 200–400. ^{13}C chemical shifts were calibrated indirectly through external adamantane (29.5 ppm relative to TMS).

Results and Discussion

In Figure 1 is shown the ^{13}C CP/MAS NMR spectrum of PG-18 at room temperature. Assignment of peaks for the CO(amide), CO(ester), C$_\alpha$, and C$_\beta$ carbons is straightforward in view of reference data for poly(γ-benzyl L-glutamate) as examined previously.[3] As for the C$_\gamma$ car-

---

† Tokyo Institute of Technology.
‡ Tokyo Kasei University.
§ JEOL Ltd.

0024-9297/88/2221-0048$01.50/0