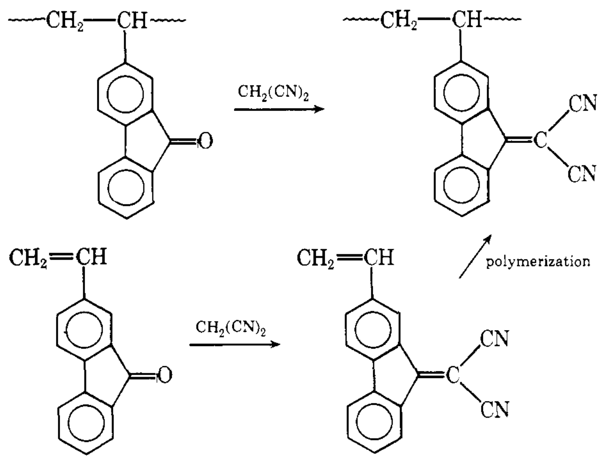
values are in the range 0.6 to 0.8, indicative of a random coil structure in these solvents. The $\bar{M}_n$ and $\bar{M}_w$ values can be determined from analysis of the gpc traces and correspond to chain extended molecular sizes based on polystyrene. The reliability of this method has been established for a number of vinyl aromatic polymers by Heller[20] and Sitaramaiah.[21]

Based on the solubility findings, the absence of any measurable insoluble materials in the polymer samples, and these molecular weight analyses it must be concluded that poly(2-vinylfluorenone) is a linear vinyl type polymer. It behaves as a typical vinyl aromatic polymer possessing a random coil configuration in some typical organic solvents.

Derivatives of Poly(2-vinylfluorenone). The carbonyl function in poly(2-vinylfluorenone) is amenable to chemistry and partial conversion into a number of novel derivatives was demonstrated, *e.g.*, reduction to the corresponding alcohol, conversion to an acetal, oxime, hydrazone,[22] etc. All of these reactions were readily carried out using conventional reagents to low, <10%, conversion. Attempts to achieve higher conversions generally created solubility problems and no attempts were made to optimize the systems.

Fluorenone is known to react readily with malononitrile, $CH_2(CN)_2$, to form 9-dicyanomethylenefluorene. Similarly treatment of 2-vinylfluorenone in methanol with malononitrile in the presence of piperidine gave a red/brown crystalline product, mp 213–215°, which was shown to be 2-vinyl-9-dicyanomethylenefluorene by spectroscopic and elemental analysis. This monomer is extremely insoluble and all attempts at free radical polymerization gave deep red insoluble polymeric products. The polymer poly(2-vinylfluorenone) also reacts to form the corresponding 9-dicyanomethylenefluorene derivative. Conversions higher than 50% resulted in formation of red, very poorly soluble, polymeric products. The copolymers containing less than approximately 50% of 2-vinyl-9-dicyanomethylenefluorene are yellow to red in color and are soluble in a number of common organic solvents.

One other interesting derivative of poly(2-vinylfluorenone) was investigated *i.e.*, a polymer containing diazofluorene functional groups. The preparation of this unique copolymer and its photochemistry are described in part II.[23] The photophysical and photochemical characteristics of poly(2-vinylfluorenone) are discussed in part III[22] of this series.



References and Notes

(1) M. Heskins and J. E. Guillet, *Macromolecules*, **3**, 224 (1970).
(2) Y. Amerik and J. E. Guillet, *Macromolecules*, **4**, 375 (1971).
(3) F. J. Golemba and J. E. Guillet, *Macromolecules*, **5**, 212 (1972).
(4) C. David, N. Putnam, M. Lempereur, and G. Geuskens, *Eur. Polym. J.*, **8**, 409 (1972).
(5) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 1405 (1970).
(6) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 537 (1970).
(7) D. Braun, *J. Polym. Sci., Part C*, **24**, 7 (1968).
(8) E. Gipstein, W. A. Hewett, and O. U. Need, *J. Polym. Sci., Part B*, **9**, 671 (1971).
(9) D. Mowry, M. Renoll, and W. Huber, *J. Amer. Chem. Soc.*, **68**, 1105 (1946).
(10) L. F. Fieser and M. Fieser,"Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1252.
(11) A. R. Lyons, *J. Polym. Sci, Part D*, 251 (1972).
(12) C. S. Marvel and O. J. Casey, *J. Org. Chem.*, **24**, 957 (1959).
(13) J. E. Mulvaney and J. G. Dillon, *J. Polym. Sci., Part A-1*, **6**, 1849 (1968).
(14) C. David, W. Demarteau, and G. Geuskens, *Polymer*, **10**, 21 (1969).
(15) D. Braun, W. Neumann, and J. Faust, *Makromol. Chem.*, **85**, 143 (1955).
(16) C. P. Pinazzi and A. Fernandez, *Makromol. Chem.*, **167**, 147 (1973).
(17) C. P. Pinazzi and A. Fernandez, *Makromol. Chem.*, **168**, 19 (1973).
(18) J. E. Mulvaney, J. G. Dillon, and J. L. Laverty, *J. Polym. Sci., Part A-1*, **6**, 1841 (1968).
(19) G. Sitaramaiah and D. Jacob, *Makromol. Chem.*, **164**, 237 (1973).
(20) J. Heller and J. Moacanin, *J. Polym. Sci, Part C*, **6**, 595 (1968).
(21) G. Sitaramaiah and D. Jacob, *Polymer*, **11**, 165 (1970).
(22) D. G. Marsh, J. F. Yanus, and J. M. Pearson, part III, submitted for publication.
(23) J. F. Yanus and J. M. Pearson, part II, submitted for publication..

Preparation and Characterization of a Monodisperse, Semiflexible Polymer, Poly(*tert*-butyl crotonate)

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ABSTRACT: If *tert*-butyl crotonate monomer is highly purified, it can be polymerized by using an anionic initiator, 2-methylbutyllithium. The experimental conditions for polymerization are studied in detail. The polymerization proceeds without termination and the molecular weight distribution of the polymer becomes monodisperse over a wide range of molecular weight. The poly(*tert*-butyl crotonate) is soluble in various solvents and shows a feature of a semiflexible chain due to steric hindrance.

Study on the polymerization of crotonic ester, $CH_3CH{=}CHCOOR$ (R = alkyl group), is meaningful from various viewpoints. There are various unsolved problems in the polymerization mechanism of α,β-disubstituted monomers, but, moreover, the polymers of crotonic esters are important in the physical chemistry of polymers. That is, they are useful for the study on configuration and conformation of ditactic polymers. The polymers of crotonic esters can

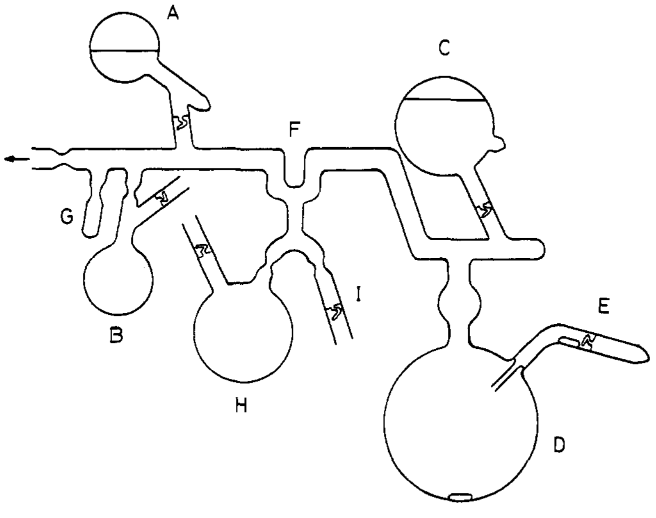

Figure 1. Purification apparatus for monomer. Symbols are shown in the text.

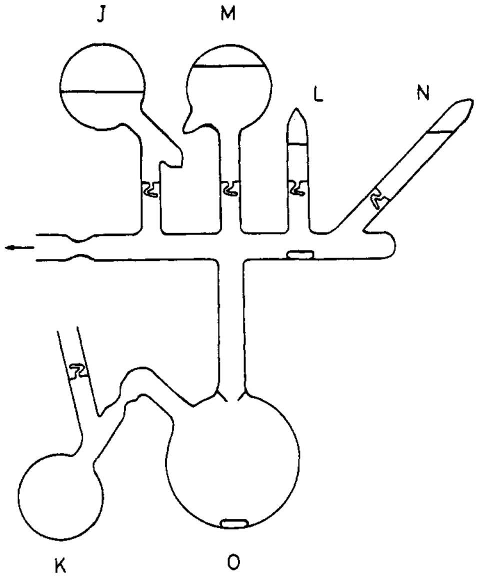

Figure 2. Polymerization apparatus. Symbols are shown in the text.

have various kinds of tactic forms, for example, threodiisotactic, erythrodiisotactic, or disyndiotactic.[1] Moreover, they may be useful for the study on the effects of β substituent on physical properties of polymer. They may have less flexible chains because of steric hindrance between α and β substituents.

The polymerization of crotonic esters, however, can effectively be carried out with neither radical nor cationic initiators, in general. They can be polymerized with anionic initiators on limited experimental conditions, but the studies on anionic polymerization of crotonic esters are very scarce in comparison with the study on acrylic or methacrylic esters. Natta, et al.,[2] first reported that branched alkyl crotonates, *i.e.*, *tert*-butyl or isopropyl esters, can be polymerized with phenylmagnesium bromide (PhMgBr) in toluene at −78°. According to Tsuruta, *et al.*,[3,4] lithium aluminum hydride and especially calcium zinc tetraethyl complex are very effective for polymerization of not only branched but also linear alkyl crotonates, such as methyl or ethyl esters, in toluene or tetrahydrofuran (THF) at −78°. However, the initiators used by Natta, *et al.*, and Tsuruta, *et al.*, are complex compounds which may generally give highly stereoregular polymers. In practice, all products obtained are crystalline and not well soluble in most ordinary solvents.

On the other hand, Miller, *et al.*,[5] used 2-methylbutyllithium (2-MeBuLi) for polymerization of *tert*-butyl crotonate (TBC) in toluene at −45° and lithium naphthalene in dimethoxyethane at −45 and 26°. They obtained almost amorphous polymers, which are soluble in toluene. Graham, *et al.*,[6] also reported that 9-fluorenyllithium, lithium naphthalene, and dibutylmagnesium can polymerize branched alkyl crotonates, especially isopropyl ester, in toluene, THF, and methylene chloride at −78°. These initiators may give less stereoregular polymers, especially in THF. In both polymerizations of Miller, *et al.*, and Graham, *et al.*, however, the conversions could not reach high and molecular weights of the polymers obtained were generally low. In particular, practically no polymerization occurred in THF. Moreover, the polymers obtained in toluene contained insoluble gel.[6] They would not be monodisperse with respect to molecular weight.

The purpose of this paper is to report that TBC can be polymerized with 2-MeBuLi in THF at −78° and the polymerization proceeds on a living mechanism, *i.e.*, with 100% conversion, to produce monodisperse polymers, *if the monomer is very carefully purified.* The polymers obtained are easily soluble in many solvents and have different configuration from the polymers polymerized with PhMgBr. Moreover, they show a feature of a semiflexible chain.

Experimental Section

(1) **Monomer.** The monomer TBC, prepared by esterification of crotonic acid in ether solution with isobutene in the presence of sulfuric acid,[7] was distilled under reduced pressure. The purity of TBC was confirmed by nmr, infrared spectrum, and gas chromatography. After drying TBC with calcium hydride, TBC was transfered to a vacuum system (about 10^{-6} mm) and purified repeatedly by distillation, treating with sodium mirror. The final purification was done with such an apparatus as is shown in Figure 1. After this apparatus was sealed off from a vacuum line, it was washed with THF solution of dipotassium salt of α-methylstyrene tetramer A, which was afterwards recovered into the vessel B and sealed off. TBC in C was transferred into flask D and *n*-butyllithium (*n*-BuLi) in *n*-hexylbenzene solution or in liquid paraffin solution was added dropwise from E to TBC in the flask D. When TBC began to polymerize, the addition of *n*-BuLi was stopped and distilled rapidly from D to H or I. The starting point of polymerization can be detected from viscous behavior of the solution. The distillation rate can be controlled by cooling trap F with a mixture of Dry Ice and acetone and trap G with liquid nitrogen. This monomer thus purified was diluted with solvents purified carefully and was used for polymerization.

(2) **Initiators.** 2-MeBuLi was synthesized by reaction of 2-methylbutyl chloride, obtained from active amyl alcohol and thionyl chloride, with metal lithium in *n*-hexane. The concentration of 2-MeBuLi in *n*-hexane solution was determined by titration with a standard hydrochloric acid solution. Besides, PhMgBr in toluene solution and *n*-BuLi in *n*-hexane solution were prepared by the usual procedures.

(3) **Solvents.** THF was purified in a previous way.[8] Toluene was first fractionally distilled after washing with sulfuric acid and drying with sodium metal wire then distilled *in vacuo* with calcium hydride as a drying agent and finally purified by distillation from a mixture with *n*-BuLi.

(4) **Polymerization.** The polymerization apparatus, as shown in Figure 2, was sealed off from a vacuum line and washed with THF solution of dipotassium salt of α-methylstyrene tetramer J, which was recovered into K and sealed off. First, the initiator solution L and then solvent M were transferred into the polymerization vessel O. After the mixture solution was cooled to a required temperature with stirring, the polymerization was started by pouring the monomer solution N instantly into O. The polymerization was continued for about 1–30 hr at the temperature. Polymerizations were mainly carried out with 2-MeBuLi in THF at −78° and, in some cases, under other conditions as shown in Table I.

The polymerization was stopped by pouring the viscous solution into excess methanol. Poly(*tert*-butyl crotonate) (PTBC) was sep-

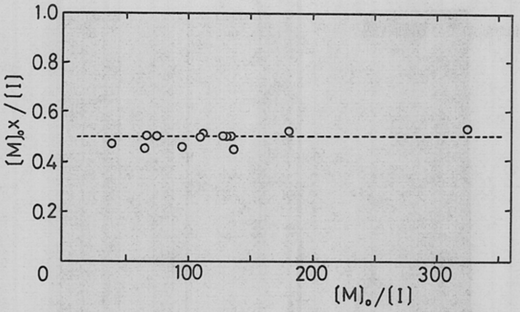

Figure 3. Initiation efficiency of 2-MeBuLi in THF. Symbols are shown in the text.

Table I
Polymerization Conditions and Solubilities of Polymers in Toluene

Polymer	Initiator	Solvent	Temp, °C	Solubility of polymer in toluene
I	2-MeBuLi	THF	−78	Soluble
II	2-MeBuLi	Toluene	−50	Partially soluble
III	*n*-BuLi	Bulk	Room temp	Soluble
IV	PhMgBr	Toluene	−78	Insoluble

arated as precipitate. The precipitate was washed with fresh methanol carefully and dried *in vacuo.* The samples for measurements of physical properties were further purified by reprecipitation and other standard techniques and then freeze dried.

(5) Characterization Methods of Polymers. PTBC thus obtained was characterized with various methods: 220-MHz nmr in deuteriochloroform at 50° with a Varian HR-220 spectrometer in the Department of Petroleum Chemistry, Kyoto University, using tetramethylsilane as a reference, infrared spectra with a JASCO IR-Al, X-ray diffraction patterns with an X-ray diffractometer of Rigakudenki Co. by the point-beam method, and DSC patterns with a Perkin-Elmer DSC-1B. The samples used were the untreated products (powder) obtained by precipitation.

Some preliminary measurements of dilute solution properties were also carried out: sedimentation patterns in cyclohexane at 35° with a Beckmann Spinco Model E, osmotic pressure measurements in toluene at 25 or 30° with a high-speed membrane osmometer, type 502, of Hewlett-Packard Co., intrinsic viscosity $[\eta]$ in toluene at 25° with a capillary viscometer of a modified Ubbelohde type, light scattering measurements in THF at 25° with an apparatus reported previously.[9] The refractive index increment in THF at 25° with 436 nm beam was determined with a Shimadzu differential refractometer to be 0.0783.

Results

(1) Polymerization. In the polymerization under the conditions as shown in Table I, the initial monomer concentration $[M]_0$ and the initiator concentration [I] are all about 0.5 and 5×10^{-3} mol/l., respectively. In the polymerization initiated with 2-MeBuLi in THF at −78°, the conversion reached as high as 80% or higher. If we continue long enough, it can reach 100%. On the other hand, in toluene at −50°, as carried out previously by Miller, *et al.*,[5] the solution becomes like a gel, but the conversion is only 20 or 30% at most. Such gel formation and low conversion are also found at all temperatures between 0 and −50°. These experimental results are in agreement with those of Graham, *et al.*[6] In bulk polymerization at room temperatures, the polymerization is almost completed in 10 min. When PhMgBr is used as an initiator, as reported previously by Natta, *et al.*,[2] the conversion is only less than 10% in about 24 hr.

The experimental conditions to study the polymerization mechanism in THF at −78° are as follows: $[M]_0$, 0.24–0.78 mol/l.; [I], 3.6×10^{-4}–1.3×10^{-2} mol/l.; THF, 80–1500 ml; polymerization time, 1.5–11.5 hr.; conversion x, 65–99%; molecular weight of polymer, 1.0×10^4–1.6×10^5. The ratio of $[M]_0x/[I]$ gives the expected molecular weight of the polymer to be compared with the observed number-average molecular weight M_n. It is found that the observed values are always twice as high as the expected values. The ratio of the expected to the observed molecular weight gives the efficiency of the initiator 2-MeBuLi in THF at −78°. The ratio is plotted against $[M]_0/[I]$ in Figure 3. It is concluded that the initiation efficiency is 0.5 on the above conditions.

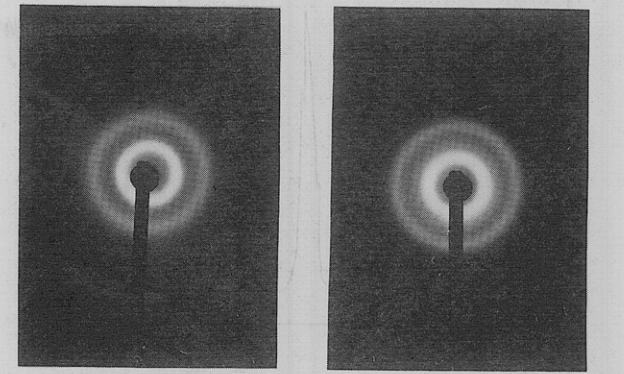

Figure 4. X-Ray diffraction patterns: a, polymer I with d spacings of 2.6 4.5, and 9.6 Å; b, polymer IV with d spacings of 2.9, 4.8, 6.4, and 11.0 Å.

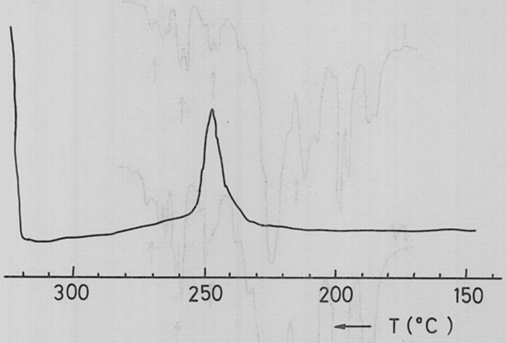

Figure 5. DSC pattern of polymer I. Chart speed is 5°C/min.

Since the conversions were changed by termination during the course of polymerization in the above experiments, the experimental results in Figure 3, together with the sharp molecular weight distribution of the polymer shown below, show that the polymerization in THF at −78° proceeds on a living mechanism.

(2) On the Configuration of Polymers. It is clear from various physical properties that polymer I, polymerized with 2-MeBuLi in THF at −78°, may have different stereoregularity from polymer IV, polymerized with PhMgBr in toluene at −78°.

Figure 4 shows the X-ray diffraction patterns for solid polymers I and IV. In both pictures, the radii of rings, that is the d spacings, are different as noted in the figure caption. Therefore, it is concluded that both groups of polymers have different crystal structures. The other polymers, polymer II, polymerized with 2-MeBuLi in toluene at −50°, and polymer III, obtained from bulk polymerization at room temperatures, give almost the same patterns as polymer I.

In Figure 5 is shown a typical DSC pattern of polymer I. Polymer IV as well as polymers II and III give almost the same patterns. The crystalline melting point is nearly 250° and degradation or decomposition of the polymer occurs at about 320°. The glass transition temperature cannot clearly be observed in our experiments.

Since we cannot find suitable solvents for polymer IV, we

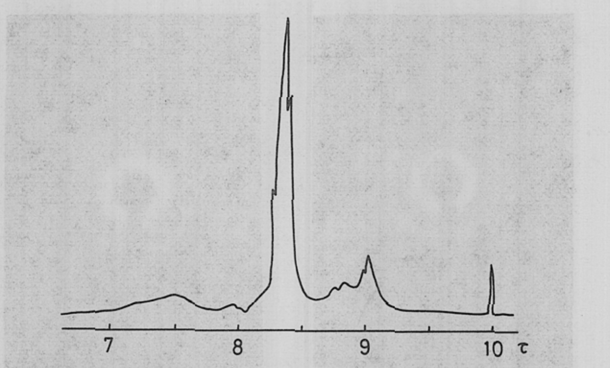

Figure 6. Nmr spectrum (220 MHz) of polymer I in 5% deuterochloroform solution at 50° using tetramethylsilane as an internal reference.

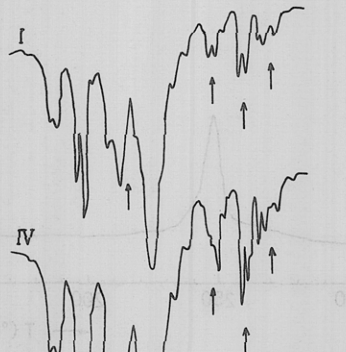

Figure 7. Infrared spectra of polymers I and IV. The arrows show markedly different parts of the spectra.

measured nmr only for polymers I, II, and III. Practically no differences are observed among them. Figure 6 shows the 220-MHz nmr spectrum of polymer I in deuterochloroform at 50°. The signals of α- and β-methine protons overlap each other to make broad peaks between τ 7.0 and 7.7. The signals of *tert*-butyl esters and β-methyl protons are found at τ 8.4 and 9.0, respectively. The ratios of the areas of these peaks are equal to 2:9:3 as expected from its chemical structure. However, the resolution of the spectrum is not high enough to obtain any information about the polymer.

On the other hand, as shown in Figure 7, infrared spectra of polymer I as well as of polymers II and III are different from that of polymer IV in the range of wave number from 700 to 1300 cm^{-1}.

Clear difference among the physical properties of various polymers is found in their solubilities in various solvents. As a typical example, solubilities of the polymers in toluene are shown in Table I.

Thus, the clear differences between polymers I and IV are found only in X-ray diffraction patterns, infrared spectra, and solubilities. However, they appear enough to show that polymer I has the same configuration as polymers II and III and a different configuration from polymer IV.

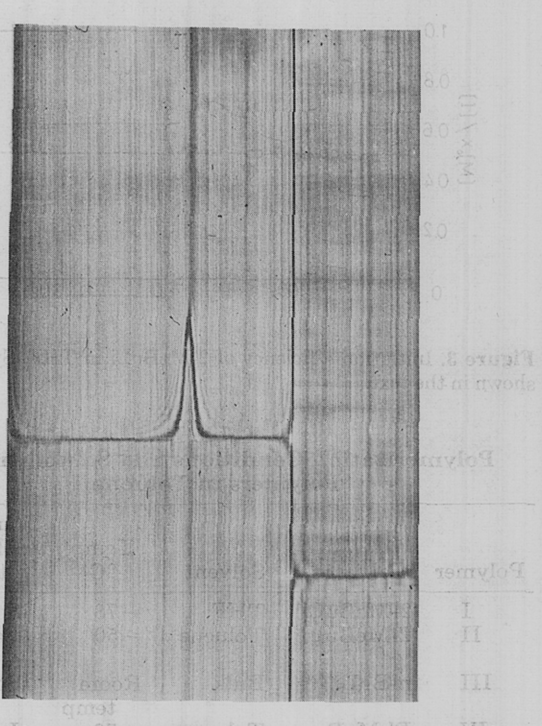

Figure 8. Sedimentation pattern of polymer I (M_n = 3.0 × 10^5) in 0.5% cyclohexane solution at 35°.

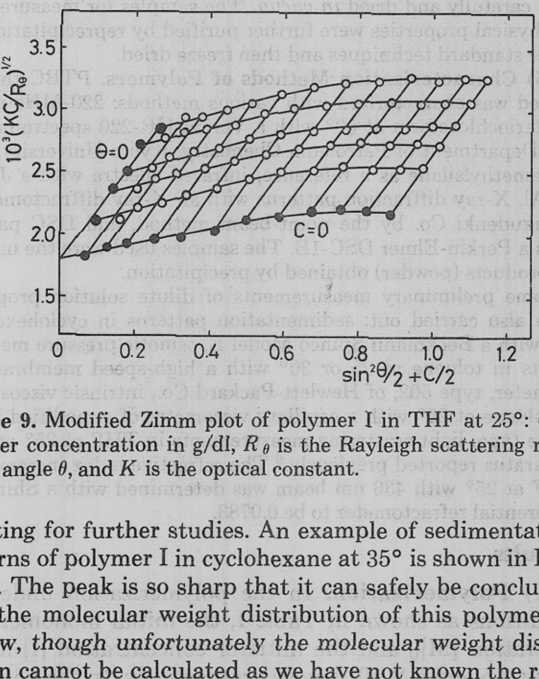

Figure 9. Modified Zimm plot of polymer I in THF at 25°: C is polymer concentration in g/dl, R_θ is the Rayleigh scattering ratio at the angle θ, and K is the optical constant.

(3) Molecular Weight Distribution and Stiffness of the Polymer. The solution properties of polymer I, polymerized with 2-MeBuLi in THF at −78°, appear to be interesting for further studies. An example of sedimentation patterns of polymer I in cyclohexane at 35° is shown in Figure 8. The peak is so sharp that it can safely be concluded that the molecular weight distribution of this polymer is narrow, though unfortunately the molecular weight distribution cannot be calculated as we have not known the relationship between sedimentation coefficient and molecular weight. Furthermore, this conclusion can be confirmed from the ratio of weight-average (M_w) and number-average molecular weights (M_n). The modified Zimm plot for light scattering and the reduced osmotic pressure *vs.* polymer concentration plot are shown in Figures 9 and 10, respectively. The results obtained are as follows: M_w = 3.06 × 10^5, M_n = 3.02 × 10^5, and M_w/M_n = 1.01.

Figure 11 shows a double logarithmic plot of $[\eta]$ *vs.* M_n. It was confirmed that the shear rate dependence of $[\eta]$ is negligible. The slope of the curve in Figure 11 gives the index a for a flexible polymer chain in the following equation

$$[\eta] = KM_n^{\,a} \qquad (1)$$

where K is usually a constant. The a is found not to be con-

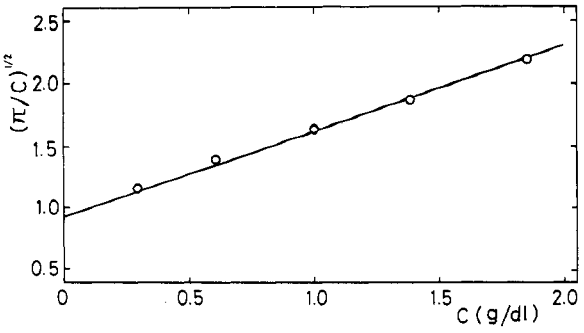

Figure 10. The square root of the reduced osmotic pressure *vs.* concentration plot of polymer I (the same sample in Figure 9): Π is osmotic pressure in g/cm^2 and C is polymer concentration in g/dl.

stant but to depend upon molecular weight in Figure 11. Especially in the molecular weight range less than 10^5, the curve is approximately linear and a is 0.96. Thus, it can be concluded that PTBC of low molecular weight has a fairly stiff backbone.

Discussion

In the polymerization of α,β-disubstituted monomers such as TBC, the steric effect may be particularly important.[10] In practice, radical polymerization of α,β-disubstituted monomers cannot effectively be carried out[5] and anionic polymerization of α,β-disubstituted monomers was reported for a limited number of monomers. This is due to the fact that in anionic polymerization the steric effect can less directly affect the propagation than in radical polymerization. In radical polymerization, the state of chain end is almost naked, whereas in anionic polymerization, coordination of chain end, counterion, and monomer may make the steric effect weak. Furthermore, in the polymerization of α,β-unsaturated carbonyl monomers, there occur usually various kinds of side reactions, such as abstraction of proton or addition to carbonyl group. In practice, the methyl or ethyl ester of crotonic acid cannot be polymerized with lithium alkyl, while TBC or isopropyl crotonate can be polymerized with various kinds of lithium alkyl, despite the fact that the polymerization of branched alkyl crotonates may be more unfavorable from the viewpoint of steric hindrance. This is due to the fact that such bulky groups of branched alkyl esters, attached to the carbonyl group, prevent the attack of the initiator or the chain end on the carbonyl group, resulting in high polymers.

The fact that the initiator efficiency is nearly equal to 0.5 in THF with 2-MeBuLi may suggest that almost half an amount of initiator may be consumed by such side reactions in the initiation or in earlier stages of the propagation. For acrylates or methacrylates, side reactions such as hydrogen abstraction or carbonyl attacks of the initiator in the stage of initiation have been investigated in detail by Tsuruta, *et al.*[11,12] In our preliminary experiments, too, where the amount of initiator 2-MeBuLi is excess ($[M]_0/[I] = 10$), isopentane was detected with gas chromatography after the polymerization is terminated with water or CO_2. However, *tert*-butyl alcohol could not be detected. Isopentane is the product from the hydrogen abstraction reaction of 2-MeBuLi, whereas *tert*-butyl alcohol is that from the carbonyl attack reaction. This fact shows that 2-MeBuLi surely abstracts hydrogen from a certain position but does not attack the carbonyl bond. These facts are very similar to the side reactions in the initiation of *n*-BuLi in the polymerization of methyl acrylate in THF.[11,12] However, once the propagation proceeds to some extent, the polymerization of TBC can proceed in a living state. It is clear from the fact that initiation efficiency is constant during the polymerization and the molecular weight of the polymer obtained is monodisperse. Strictly speaking, however, it is not clear whether or not initiator efficiency in the present experiments arises only from the same cause as in the experimental results of Tsuruta, *et al.* It appears somewhat unreasonable to assume that the hydrogen abstraction reaction of the initiator would occur only in the initiation stage. Unfortunately, the quantitative measurement of isopentane could not be carried out in the present experiments because of too low concentration of the initiator. Moreover, it may be worth while noting that the same initiator efficiency (0.5) was also found in the polymerization of α-methylstyrene with *n*-BuLi in THF, where proton abstraction does not occur.[8]

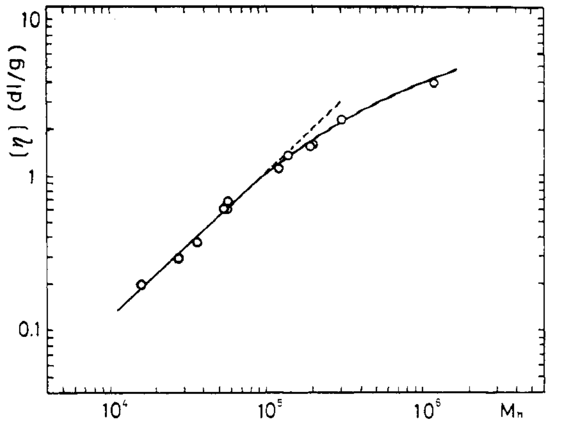

Figure 11. The double logarithmic plot of intrinsic viscosity in toluene at 25° *vs.* molecular weight of polymer I.

With 2-MeBuLi, some clear differences can be observed between the polymerization in toluene and in THF. In toluene, the initiator 2-MeBuLi is in the state of association or poor dissociation, while in THF it can be expected to dissociate highly, although it may be solvated. Therefore, the effective initiator concentration in toluene is less than in THF at the same concentration of the initiator, so that a higher molecular weight polymer may be obtained in toluene than in THF. The gelation in the course of polymerization in toluene may be due to this high molecular weight in addition to semiflexibility of PTBC, because any differences of tacticities cannot be found between the polymers I and II.

It is clear from the studies on X-ray diffraction patterns, infrared spectra, and solubilities that polymers I, II, and III have the same configuration, whereas polymer IV has a different configuration from others. The difference in the solubilities may not necessarily be due to the difference in their configurations. The solubility can depend on both tacticity and molecular weight of polymers. However, it is unlikely that the molecular weight of sample IV is so unusually high, considering the ratio of the initiator amount to the monomer amount. It may be concluded that the poor solubility of polymer IV is due to its high stereoregularity.

The polymer PTBC is considered to have a semiflexible chain, from the fact that the index a in eq 1 is nearly unity in the range of $M < 10^5$. This value of a is less than that of poly(n-butyl isocyanate)[13] but comparable to those of cellulose derivatives,[14] both of which are typical "stiff chains." The semiflexibility of PTBC is due to the fact that the methyl groups at β position and the *tert*-butyl ester groups at α position restrict the internal rotation around the C–C bond of the main chain to a large extent and stretch the whole chain strongly in a certain direction. So far as we know, this may be the first sample which has a semiflexible backbone and is monodisperse with respect to molecular weight.

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References and Notes

(1) G. Natta, M. Farina, and M. Peraldo, *J. Polym. Sci.,* **43,** 289 (1960).

(2) G. Natta, M. Peraldo, and M. Farina, Belgian Patent 599,833 (1961), U.S. Patent 3,259,612 (1966).

(3) T. Tsuruta, T. Makimoto, and T. Miyazako, *Makromol. Chem.,* **103,** 128 (1967).

(4) T. Tsuruta, T. Makimoto, and K. Tanabe, *Makromol. Chem.,* **114,** 182 (1968).

(5) M. L. Miller and J. Skogman, *J. Polym. Sci., Part A,* **2,** 4551 (1964).

(6) R. K. Graham, J. E. Moore, and J. A. Powell, *J. Appl. Polym. Sci.,* **11,** 1797 (1967).

(7) A. L. McCloskey, G. S. Fonken, R. W. Kluiber, and W. S. Johnson, *Org. Syn.,* **34,** 26 (1954).

(8) T. Fujimoto, N. Ozaki, and M. Nagasawa, *J. Polym. Sci.,* **3,** 2259 (1965).

(9) T. Kato, A. Takahasi, M. Nagasawa, and I. Kagawa, *Nippon Kagaku Zasshi,* **88,** 524 (1967).

(10) T. Tsuruta in "Structure and Mechanisms in Vinyl Polymerization," T. Tsuruta and K. F. O'Driscoll, Ed., Marcel Dekker, New York, N.Y., 1969.

(11) N. Kawabata and T. Tsuruta, *Kogyo Kagaku Zasshi,* **68,** 340 (1965).

(12) N. Kawabata and T. Tsuruta, *Makromol. Chem.,* **86,** 231 (1965).

(13) W. Burchard, *Makromol. Chem.,* **67,** 182 (1963).

(14) E. Penzel and G. V. Schulz, *Makromol. Chem.,* **113,** 64 (1968).

Stereoelective Polymerization of DL-Amino Acid *N*-Carboxyanhydrides by Nickel *d*-2-Methylbutyrate–Tri-*n*-butylphosphine Catalyst System

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ABSTRACT: The polymerization of *N*-carboxyanhydride of γ-benzyl DL-glutamate or of DL-alanine by the nickel *d*-2-methylbutyrate–tri-*n*-butylphosphine catalyst system proceeded stereoelectively to give an optically active polymer of high molecular weight. The monomer whose absolute configuration is identical with that of the asymmetric carbon in the acyloxy group of the catalyst system was polymerized preferentially.

The characteristic behavior of the $Ni(OAc)_2 \cdot 4H_2O$-*n*-Bu_3P catalyst system exhibited in the polymerization of γ-benzyl L-glutamate NCA (L-BG-NCA) was ascribed to the active participation of the nickel salt in the propagation step.[2] This interpretation was subsequently substantiated by experimental results which indicated that the DL-copolymerizations of mixtures composed of various ratios of L- and DL-BG-NCA by the (*dl*-$C_2H_5(CH_3)CHCOO)_2Ni$-*n*-Bu_3P catalyst system (*dl*-Ni catalyst) were controlled stereochemically more effectively than by the simple amine catalyst.[3] In fact, the stereoregularity of the DL-copolymer prepared by the former catalyst, which was determined by the regular helix content, was far higher than that by the latter one.[3] Kinetic analysis of the polymerization process of DL-BG-NCA or DL-alanine NCA (DL-Ala-NCA) by the *dl*-Ni catalyst also revealed that these polymerization reactions proceeded stereospecifically.[3]

As a logical extention of these experiments, the stereoelective polymerization was applied to DL-BG-NCA having a rather long side chain or DL-Ala-NCA having the shortest side chain. The polymerization of a DL-NCA with the optically active Ni catalyst was suggested to give an optically active polymer. In fact, this expectation was found to give satisfactory results in our work. This paper deals with these experimental results.

The stereoelective polymerization of DL-Ala-NCA or DL-leucine NCA was reported by other workers with the $AlEt_3$–borneol catalyst system[4,5] or optically active amines,[6] but unfortunately specific rotations and molecular weights of their polymers were not sufficiently high values.

Experimental Section

Materials. NCAs, nickel carboxylates, and other reagents were prepared and/or purified by the methods described in preceding papers.[2,3]

Nickel *d*-2-methylbutyrate was prepared as follows. *d*-2-Methylbutyric acid was prepared by oxidizing optically active amyl alcohol (2-methylbutanol) in basic solution[7] and was purified by fractional distillation using Tokyokagakuseiki Model HSB-805E Spinning Band Rectifier: bp 175–177°; $[\alpha]^{20}{}_D$ +17.2° (neat) (lit. $[\alpha]_D$ +19.33°).[8] *d*-2-Methylbutyric acid was transformed to nickel *d*-2-methylbutyrate in the same manner as described for nickel *dl*-2-methylbutyrate:[3] $[\alpha]^{20}{}_{577}$ +4.4° (dichloroacetic acid (DCA), *c* 2.71 g/100 ml), $[\alpha]^{20}{}_{546}$ +6.8° (DCA, *c* 2.71 g/100 ml), $[\alpha]^{20}{}_{577}$ −1.8° (THF, *c* 6.76 g/100 ml), $[\alpha]^{20}{}_{546}$ −2.2° (THF, *c* 6.76 g/100 ml). *Anal.* Calcd for $C_{10}H_8O_4Ni$: C, 45.9: H, 6.90. Found: C, 45.81; H, 6.26.

Solvents. Anisole was refluxed over CaH_2 for 24 hr, refluxed over metallic sodium for 24 hr, and then distilled under an anhydrous argon atmosphere (bp 155°). Other solvents were purified by the methods described in preceding papers.[2,3]

Polymerization. Polymerizations were carried out by the methods described in preceding papers.[2,3] The polymerization of DL-BG- or of DL-Ala-NCA was terminated by adding 100 ml of ethanol to 10 ml of the polymerization medium. By this treatment, unreacted NCA and catalyst system were almost completely removed from the polymer. The yield of polymer was determined gravimetrically. The polymer obtained was washed twice with 100 ml of diethyl ether and dried at 80° for 12 hr *in vacuo*. To remove the free amino acid, catalyst system, and other optically active substances as completely as possible from the polymer, poly(γ-benzyl glutamate) (P-BG) was reprecipitated twice from dioxane (20 ml)–diethyl ether (200 ml) or poly(alanine) (P-Ala) was reprecipitated twice from DCA (5 ml)–diethyl ether (200 ml).

Kinetic Measurements. Polymerization reaction was followed by measuring the intensity of the infrared absorption band at 1850 cm^{-1}, which is assigned to the 2-carbonyl group in the NCA ring, using a JASCO Model DS-402 spectrometer in a 0.1 mm thickness of KBr in a liquid cell under an argon atmosphere. Weak absorption bands due to the solvent (THF) were compensated for using the reference cell. $[M_0]/[M_t]$ is referred to the monomer concentration at the time zero and *t*. v_0 represents the rate of monomer consumption, which is calculated by the equation $-d[M]/dt$.

Characterization of the Polymer. ORD of the polymer was measured in 20- or in 50-mm cells using a Yanagimoto ORD Model 185 or a JASCO Model J10 Automatic Polarimeter. Specific rota-