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# High-Resolution Carbon-13 Nuclear Magnetic Resonance of Trigonal and Orthorhombic Crystals of Poly(oxymethylene)

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ABSTRACT: $^{13}$C NMR spectra of a needlelike single crystal of trigonal poly(oxymethylene) (t-POM) have been investigated in comparison with those of ordinary semicrystalline samples of t-POM. The $^{13}$C signal in the single crystal splits into a doublet at 88.5 and 87.7 ppm in contrast to the singlet at 88.4 ppm in the semicrystalline samples. The split pattern is ascribed to the inequivalent monomeric units in the crystal field of the t-POM lattice. The corresponding $^{13}$C signal of a plate-shaped single crystal of orthorhombic POM (o-POM) appears at 82.0 ppm as a singlet as anticipated from the space group of o-POM. The large chemical shift difference (6 ppm) between t-POM and o-POM was interpreted in terms of the intramolecular $\gamma$-gauche shielding and the intermolecular packing effect.

## Introduction

Since the pioneering works of Schaefer and Stejskal[1–3] in the field of solid-state, high-resolution $^{13}$C NMR spectroscopy of polymers, application of this method to the structural studies of crystalline polymers is rapidly increasing.

The present study is concerned with fine structure in the high-resolution $^{13}$C NMR spectra due to the inequivalent carbon atoms in the trigonal phase of poly(oxymethylene) and the difference in the isotropic $^{13}$C chemical shift between the trigonal and orthorhombic phases. Poly(oxymethlene) (abbreviated as POM) is one of the typical crystalline linear polymers having a simple chemical structure $(CH_2O)_n$. There are two crystal modifications: the trigonal (t-POM) and orthorhombic (o-POM) forms. The trigonal form is stable at ambient conditions and is obtained exclusively through the ordinary crystallization procedures from the melt and dilute solutions. The orthorhombic form is metastable at ambient conditions and transforms to the trigonal form by heating above 69 °C.[4,5] The o-POM samples are obtained by some specific polymerization processes.[6–8]

The high-resolution $^{13}$C NMR spectrum (measured at 45 MHz) of t-POM has been studied first by Veeman et al.[9] by means of the proton-decoupled magic-angle-spinning (MAS) technique with and without cross-polarization (CP). They demonstrated that the t-POM sample (a Delrin resin of E. I. du Pont de Nemours and Co., Inc.) gave rise to a singlet signal at about 90 ppm (measured from TMS) with a line width of 3.7–5.7 ppm depending on the MAS frequency. The measurement of $T_1$ and $T_{1\rho}$ of $^{13}$C indicated the coexistence of two phases: a crystalline phase having short $T_{1\rho}$ and long $T_1$ and an amorphous phase with a longer $T_{1\rho}$ and a shorter $T_1$. Cholli et al.[10] measured $^{13}$C CP-MAS NMR spectra (measured at 37.7 MHz) of a semicrystalline t-POM sample. Although the $^{13}$C signal was not resolved into the crystalline and amorphous components, the amorphous $^{13}$C resonance was isolated from the crystalline one by the aid of difference in relaxation behavior (by means of a modified CP-MAS technique). They concluded that the amorphous $^{13}$C peak appeared at about 1 ppm downfield compared to the crystalline peak. Kurosu et al.[11] measured the $^{13}$C CP-MAS NMR spectra (measured at 67.8 MHz) of t-POM on various samples obtained from a commercial resin (Tenac 7010 of Asahi Chem. Ind. Co., Ltd.) treated by different crystallization procedures. They observed a singlet signal centered at 88.5 ppm. The observed band profile was simulated by two Lorentzian functions centered at 88.5 and 89.4–91.5 ppm (depending on the crystallinity of the samples), the former and the latter being ascribed to the crystalline and amorphous phases, respectively. They also measured the powder pattern spectra of the same samples and derived the values of the elements of the chemical shift tensors of the crystalline and amorphous phases. Thereafter, Kurosu et al.[12] measured $^{13}$C CP-MAS and powder pattern spectra of a POM sample which contained a small amount of o-POM, the major component being t-POM, and evaluated the isotropic $^{13}$C chemical shift of o-POM.

Thus, in the previous papers, the carbon atoms in the

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crystalline phase of t-POM (and in o-POM as well) have been treated as being equivalent to each other and having the same chemical shift tensor. Strictly speaking, as will be discussed below, the equivalence is not held true in the case of t-POM from the crystallographic viewpoint, and it is anticipated that a band splitting due to the inequivalence is detectable, if the resolution is high enough and the crystal order of the sample is extremely high.

In order to confirm experimentally the above prediction, we measured, in the present work, $^{13}C$ high-resolution CP-MAS spectra of t-POM on a specially prepared sample consisting of highly ordered crystals using a spectrometer operating at a frequency as high as 100 MHz. The results are compared with those measured on ordinary semicrystalline samples.

The $^{13}C$ spectral data of o-POM published in ref 12 are rather ambiguous because of very small amount of the orthorhombic phase contained in the sample used. Therefore, the spectrum of o-POM is also reinvestigated on a POM sample containing a larger amount (about 10 mol %) of single crystals of this form. The difference in the isotropic $^{13}C$ chemical shift between t-POM and o-POM is considered in relation to the difference in structure.

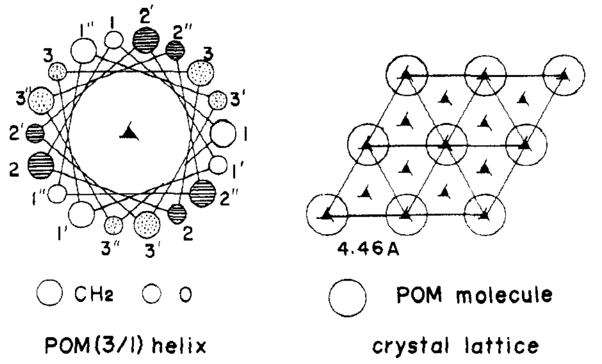
## Experimental Section

**Samples.** A powder sample, which is an assembly of fine needlelike single crystals, of t-POM was prepared in the Research Institute for Polymers and Textiles through a heterogeneous cationic polymerization of trioxane.[13,14] Each single crystal has a hexagon pillar shape of about 100 μm in length and a few microns in width. In a previous paper,[7] it was demonstrated that plate-shaped single crystals of o-POM (30–50 μm in diameter and about 2 μm in thickness), which occupied about 10 mol % of the mixture with t-POM crystals, were obtained in a special batch which had been originally designed to prepare only needlelike crystals of t-POM. The orthorhombic modification of the plate-shaped crystals was identified by microfocus Raman spectroscopy and X-ray diffraction,[7] and the orientation of the crystallographic axes was determined by the polarized Raman and FT-IR microprobe measurements combined with the normal modes calculation.[15-17] The same sample of the mixture of t-POM and o-POM was used in the present work. A t-POM powder sample crystallized from a 0.5 wt % bromobenzene solution at 130 °C and a commercial film sample of t-POM were investigated for comparison.

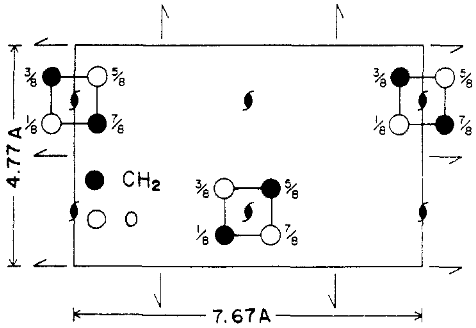
**NMR Measurements.** $^{13}C$ CP-MAS spectra were measured at ambient by using a JEOL GSX-400 NMR spectrometer operating at 100.4 MHz and equipped with a CP-MAS accessory. Powder samples were contained in a bullet-type rotor and spun at 5–6 kHz. In the CP pulse sequence, the contact time of $^{13}C$ with polarized proton power (irradiated with 90° pulse for 5.2 μs) was 0.5–3.0 ms, and the pulse duration was 4.5–20.0 s. The spectral width and the data points were 40 kHz and 8K (or 16K), respectively. Spectra were accumulated 1000–28000 times depending on the required signal-to-noise ratio. The $^{13}C$ chemical shifts were calibrated through external adamantane (29.50 ppm measured from tetramethylsilane (TMS)).

In the first stage of this work, we used a Varian XL-300 ($^{13}C$: 75.4 MHz) spectrometer. Since the results obtained were essentially the same as those obtained with JEOL GSX-400, the latter are mainly presented here.

## Results and Discussion



(a) t-POM



(b) o-POM

**Figure 1.** Crystal structures and space group symmetries of trigonal and orthorhombic poly(oxymethylene): (a) (3/1) helix of POM molecule whose asymmetric unit consists of three crystallographically inequivalent chemical units (1–2–3, 1′–2′–3′, or 1″-2″-3″) (left) and the trigonal crystal lattice with the space group $P3_1$ (right); (b) orthorhombic crystal lattice with the space group $P2_12_12_1$ which consists of (2/1) helices.

**Structures and Predicted NMR Spectra of t-POM and o-POM.** In the unit cell of t-POM, one molecular chain passes through having a (9/5) helical conformation, which means that nine chemical units make up one fiber identity period of 1.73 nm and turn 5 times around the fiber axis. The space group is $P3_1$ with a threefold screw symmetry.[18,19] In the uniform (9/5) helix which has a ninefold screw symmetry, all the chemical units are equivalent to one another. However, in the crystal lattice, presence of ninefold symmetry is not permitted from the crystallographic viewpoint. In fact, the space group of t-POM is $P3_1$ with a threefold screw symmetry as illustrated in Figure 1a.[18,19] Thus, the molecule in the trigonal lattice has a threefold screw axis instead of a ninefold screw axis. Therefore, strictly speaking, the t-POM molecule should be recognized as a (3/1) helix, consisting of the asymmetric units of $CH_2O{\cdot}CH_2O{\cdot}CH_2O$. Three carbon atoms (or methylene units) in one asymmetric unit are inequivalent to one another, as sketched differently in Figure 1a. Thus, there are three crystallographically inequivalent methylene sites in the t-POM lattice. Consequently, the $^{13}C$ signal due to the crystalline phase can potentially be split into three components.

The splitting of $^{13}C$ signals caused by such inequivalent chemical units of a polymer molecule put in a crystal lattice has been detected for the α-form of isotactic polypropylene (IPP),[20] where the $^{13}C$ resonance absorptions due to the $CH_2$ and $CH_3$ groups exhibit well-resolved doublets with a band gap of 1.0 and 0.5 ppm, respectively. In this case, the inequivalence arises from the interchain packing of (3/1) helices adopted in a monoclinic lattice (there is no threefold screw symmetry in the lattice). The splitting becomes undetectable in a poorly crystalline sample. Judging from the cylindrically more symmetric molecular structure of t-POM than the (3/1) helix of IPP, the band gap due to the above-mentioned inequivalence is considered to be smaller than that of

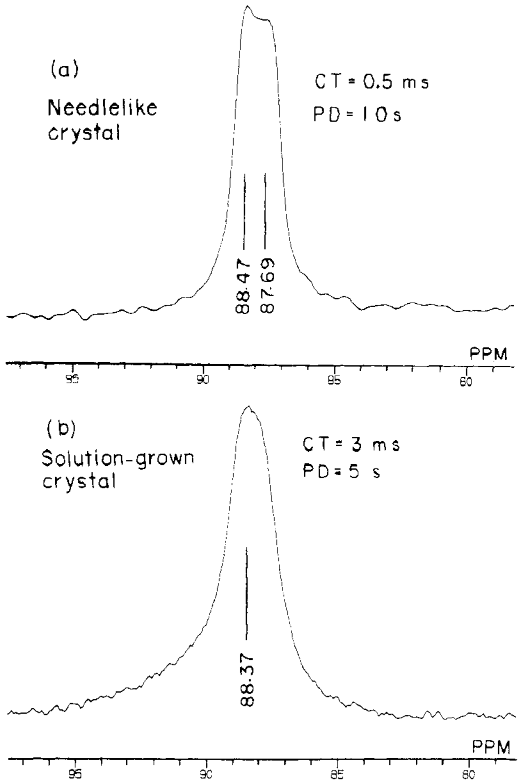


**Figure 2.** $^{13}C$ CP-MAS NMR spectra (100.4 MHz at room temperature) of (a) needlelike single crystal and (b) solution-grown sample of trigonal poly(oxymethylene), measured with contact time (CT) and pulse duration (PD) indicated.

the $\alpha$-form of IPP. Therefore, the presence of crystal disorders in ordinary semicrystalline samples smears the split pattern into a singlet, as is seen in the $^{13}C$ CP-MAS spectra so far reported. One of the aims of the present work is to detect the splitting, if any, of the $^{13}C$ resonance of t-POM measured on needlelike single crystals having an extremely high crystal perfection.

In o-POM, two (2/1) helical molecules having the fiber period of 0.356 nm pass through the unit cell of the space group $P2_12_12_1$. Any two of four chemical units contained in the unit cell are related to each other by one of the twofold screw rotations described in Figure 1b, so that all the units are equivalent to each other in the strict sence.[6] Therefore, the $^{13}C$ signal of the o-POM crystal should be singlet.

**Spectral Characteristics of a t-POM Single Crystal.** The $^{13}C$ CP-MAS spectra of the needlelike crystal (sample A) and the solution grown sample (sample B) of t-POM are compared with each other in Figure 2. In sample B, there appears a singlet signal centered at 88.4ppm with a small downfield shoulder (Figure 2b). The spectral pattern is the same as those reported in refs 9, 11, and 12. A film sample of POM resin gives rise to a similar spectrum. The band profile is simulated by two Lorentzian functions centered at 91.1 ppm (due to the amorphous phase with relative intensity 0.11) and 88.4 ppm (due to the crystalline phase with relative intensity 0.89) having full width at half-height (fwhh) of 3.0 and 2.0 ppm, respectively. On the contrary, sample A gives rise to a different spectral pattern; the signal splits into two (or three) components centered at 88.5 and 87.7 ppm, and there is no downfield shoulder due to the amorphous phase (Figure 2a). The lack of the shoulder is quite reasonable since sample A is an assembly of single crystals (whiskers). The split pattern of the crystal signal of t-POM is found for the first time, as far as we know, and might be ascribed to the inequivalence of the carbon atoms in the crystal field of the trigonal lattice. Although a triplet pattern just as intense is anticipated from the $P3_1$ space group, the observed spectrum is deformed from that. The observed band profile is simulated tentatively by two Lorentzian functions centered at 88.5 (relative intensity 0.53) and 87.7 (0.47) ppm with the same fwhh of 1.1 ppm. It is noted that the position of the 88.5 ppm component coincides with that of the crystal signal found in the ordinary t-POM samples, while the 87.7 ppm component appears only in the highly ordered crystal.

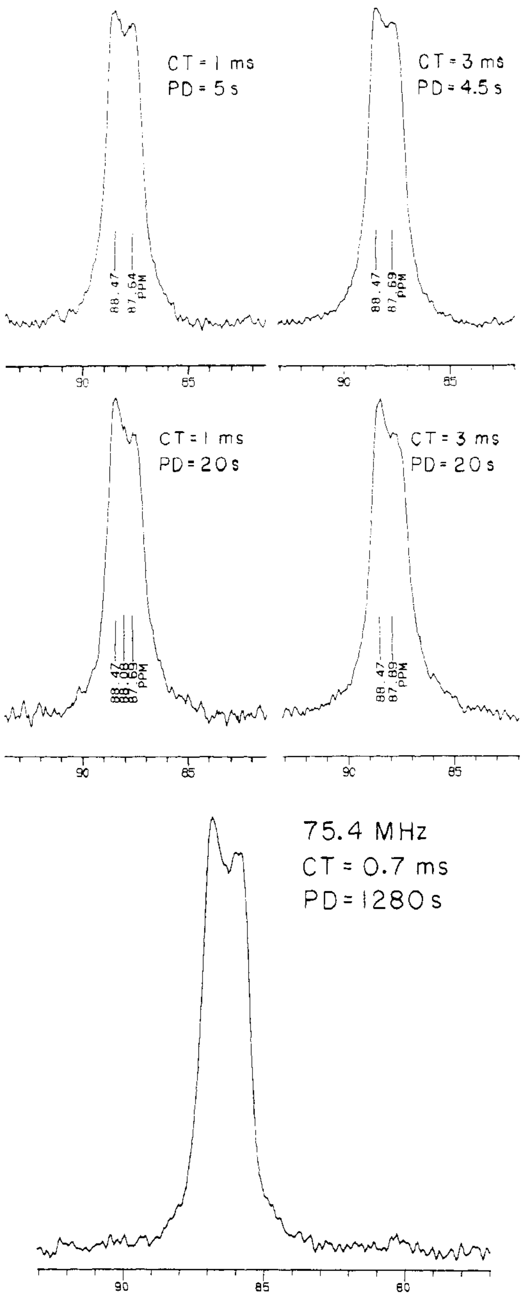


**Figure 3.** $^{13}C$ CP-MAS NMR spectra of needlelike crystal of trigonal poly(oxymethylene) measured at room temperature with different sets of contact time (CT) and pulse duration (PD): (a) 100.4 MHz, (b) 75.4 MHz.

In the CP-MAS experiment, the spectral pattern changes more or less with the condition of the pulse sequence. In order to check this effect, the spectrum of sample A was measured with different pulse duration (PD) ranging from 4.5 to 20 s and different contact times (CT) ranging from 0.5 to 3.0 ms. Although the relative intensities of the split components depend a little on PD, a similar splitting is observed in every case as shown in Figure 3a. In

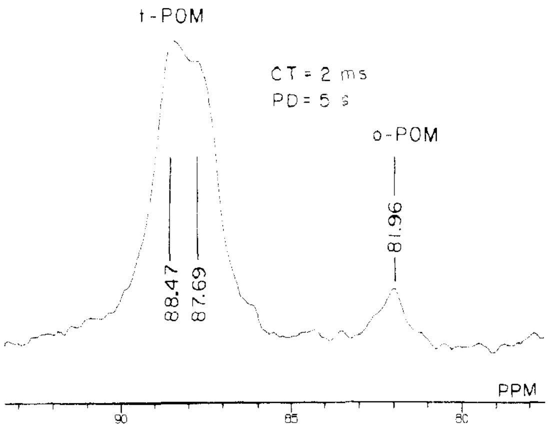


**Figure 4.** $^{13}C$ CP-MAS NMR spectra (100.4 MHz at room temperature) of a mixture of single crystals of trigonal and orthorhombic poly(oxymethylene).

the CP experiment, the optimum PD time is on the order of 5 times the $^1H$ $T_1$ value. Since a rather long $^1H$ $T_1$ of 131–137 s was obtained (by a 90–180° pulse method) for sample A, a CP-MAS spectrum was measured with a far longer PD (1280 s) as shown in Figure 3b. The spectral pattern obtained is similar to those obtained with PD = 20 s. On the basis of these experimental results, we conclude that the split pattern is recognized as characteristic of the highly ordered crystal of t-POM.

In ref 5, we demonstrated that in the t-POM lattice at ambient temperature there should be a rotational molecular motion around the chain axis. If such a rotational fluctuation takes place in a random way, all the chemical units might be averaged to be equivalent on the time scale of $10^8$ Hz. Therefore, the appearance of the split pattern in the $^{13}C$ NMR spectrum suggests that the rotation takes place with a correlation among the neighboring molecules.

**$^{13}C$ Spectrum of o-POM.** In order to obtain the $^{13}C$ CP-MAS spectrum of o-POM, the mixture of single crystals of t-POM and o-POM (see Experimental Section) was subjected to the measurement as shown in Figure 4. In addition to the doublet at 88.5 and 87.7 ppm due to the t-POM crystal, there appears a singlet at 82.0 ppm due to the o-POM crystal. The singlet pattern of the latter is consistent with the unit-cell structure of o-POM. Kurosu et al. reported the value of the isotopic chemical shift of o-POM as 86.0 ppm.[12] In their spectrum, however, there is no distinct o-POM signal well resolved from the major t-POM signal, and the o-POM component has been separated from the upfield wing of the major signal by curve fitting. The absence of the 82.0 ppm signal is probably caused by the small content of o-POM in their sample. Thus, the value of the $^{13}C$ isotropic chemical shift should be revised as presented here.

It should be noted that there is a big difference in the isotropic $^{13}C$ chemical shift between t-POM and o-POM. The dependence of $^{13}C$ chemical shift on chain conformation in the solid state has been interpreted in terms of an empirical rule: "3-bond interactions" or "$\gamma$-gauche shielding effect".[21] For example, the spectral features of crystalline isotactic[20] and syndiotactic polypropylenes[22] as well as three crystal modifications of isotactic poly(1-butene)[23] have been explained on the basis of this rule. The $^{13}C$ chemical shift of o-POM is markedly different (upfield shifted by about 6 ppm) from that of t-POM, despite the fact that the molecules in both crystalline forms have a similar ($g_2$) conformation. The difference in the backbone dihedral angle (77°23′ for t-POM[18,19] and 63°41′ for o-POM[6]) may partly be responsible for the observed chemical shift difference; more intense $\gamma$-gauche shielding is predicted for o-POM than t-POM, as has been pointed out by Schilling et al.[23] for the case of three crystalline forms of poly(1-butene). However, in poly(1-butene), the change in the $C_\alpha$–$C_\beta$ dihedral angle from 83° (form III) to 60° (form I) produces an upfield shift of 4.5 ppm for the $\alpha$-CH resonance, whereas in POM a smaller change in the dihedral angle produces a bigger change in the $^{13}C$ chemical shift. The difference in $\angle$COC ($=\angle$OCO) valence angle between t-POM (110°53′) and o-POM (112°41′), and also the difference in intermolecular packing, may contribute the observed large chemical shift difference, similar to the case of two crystalline forms of poly(3,3-diethyloxetane).[24]

Recently, Kurosu et al.[25] investigated the interchain effect of POM on the $^{13}C$ chemical shift by means of the tight-binding MO calculations. Since the values of the azimuthal angle as well as the relative height of t-POM chains in the unit cell are not known, the calculations have been performed for various sets of these chain-packing parameters, and the results have been compared with those of o-POM calculated by using the crystallographic parameters reported by Carazzolo and Mammi.[6] The difference in the isotropic $^{13}C$ chemical shift $\sigma_{iso}$ between t-POM and o-POM depends significantly on the interchain packing parameters and varies from −2.0 to 8.2 ppm (the positive sign means the upfield shift of $\sigma_{iso}$ in o-POM compared to t-POM). The corresponding value due to the intramolecular effect (mainly caused by the $\gamma$-gauche shielding) is 2.8 ppm. Thus, the observed chemical-shift difference (6 ppm) may be interpreted by considering the interchain packing effect in addition to the $\gamma$-gauche effect.

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# $^{13}$C NMR Structural Studies of a Soluble Polydiacetylene Poly(4BCMU)

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ABSTRACT: The chromism of a soluble polydiacetylene, poly(4BCMU), whose side chain substituents are $(CH_2)_4OOCNHCH_2COO(CH_2)_3CH_3$, was studied by use of high-resolution, solid-state $^{13}$C NMR spectroscopy. The solid-state thermochromic transition (104 °C; DSC at 10 °C/min) resulted in a more localized electronic state for the backbone, extended side chains with more trans bond character, and retention of the hydrogen-bonding network between side chains, results similar to those observed for the thermochromic transition of poly(ETCD), whose side chains are $(CH_2)_4OOCNHCH_2CH_3$. Unlike poly(ETCD), the thermochromic transition observed in poly(4BCMU) was irreversible, and poly(4BCMU) cooled from the red phase or molten state to room temperature displayed two distinct backbone structures. Melting poly(4BCMU) (132 °C; DSC at 10 °C/min) caused a weakening of the hydrogen bonds or possibly the formation of intermolecular hydrogen bonds. A solid, red gel of poly(4BCMU) in toluene-$d_8$ and a liquid, yellow–orange solution of poly(4BCMU) in $CDCl_3$ were found to have backbone electronic states observable by solid-state $^{13}$C NMR. The absence of both the butatrienic form of backbone conjugation and a trans to cis isomerization of the backbone double bonds was demonstrated. Backbone electronic and motional states and the conformations, motions, and hydrogen bonding of the side chains of poly(4BCMU) in the solid state and in solvents were found to be consistent with a model that suggests the thermochromic phase transition in polydiacetylenes may result from the strain placed on the backbone by its side chains.

## Introduction

Polydiacetylenes are an unusual class of polymers because their solid-state polymerization from crystallized monomers can produce macroscopic single crystals of polymer.[1] The polymerization proceeds by 1,4-addition and results in polymers with conjugated backbones as illustrated in Figure 1a. Extensive delocalization of $\pi$-electrons along the backbone gives polydiacetylenes interesting optical properties[1–4] and is also responsible for their absorption of light in the visible range. External influences, such as mechanical or thermal stress, can alter the amount of $\pi$-electron delocalization, thereby changing the absorption properties of polydiacetylenes, which are well-known for their characteristic chromism.

Though most polydiacetylenes are insoluble, several form solutions in common organic solvents. One such soluble polydiacetylene was first synthesized[5,6] in 1978 from 5,7-dodecadiyne-1,12-diol bis[((butoxycarbonyl)methyl)urethane] and is commonly called poly(4BCMU) (see Figure 1b). The initial portion of the poly(4BCMU) side chain is identical with the side chains of other insoluble polydiacetylenes, such as poly(ETCD) (R = $(CH_2)_4OOCNHCH_2CH_3$) and poly(TCDU) (R = $(CH_2)_4OOCNHC_6H_5$). Apparently the longer side chains of poly(4BCMU) contribute enough conformational entropy to allow solubility in solvents like chloroform, nitromethane, and toluene.[1]

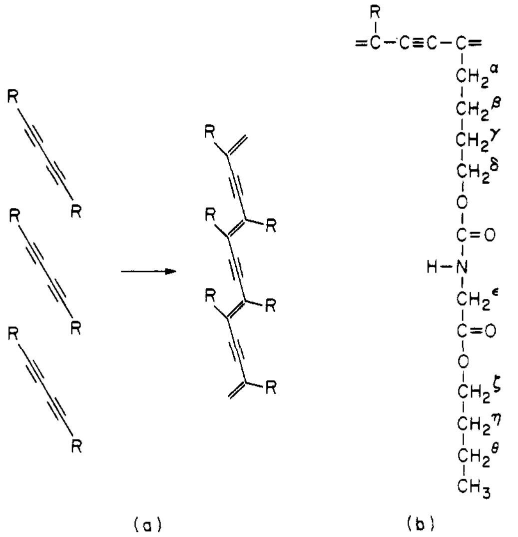

**Figure 1.** (a) Schematic representation of the solid-state synthesis of polydiacetylenes. (b) Chemical structure of poly(4BCMU).

Poly(4BCMU) displays chromic transitions in its crystalline and solution-cast film solid states and also in solu-

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