Macromolecules 1988, *21*, 1234–1238

In closing we would like to point out the possible implications of our work in phenomena involving synthetic polymers which do not exhibit liquid crystalline order or perhaps in biopolymers such as proteins and DNA. Phase separation related to conformational characteristics of sequences in chemically disordered polymers may occur frequently but go undetected by current experimental methods. If the system does not have the molecular characteristics that lead to mesophase formation, it may fail to produce the contrast necessary for detection or may simply phase separate with exceedingly slow kinetics. Slow kinetics may occur in systems where the conformational differences produced by chemical disorder are rather small compared to those between chains in isotropic versus nematic phases. Proteins are of course very specific chemical sequences of amino acids just as DNA macromolecules have specific sequences of nucleotides. However, in biological systems proteins or polynucleotides may occur as blends of many different molecules which differ in chemical sequence but contain similar structural units. In this context, a mixture of proteins or polynucleotides becomes analogous to the chemically disordered system studied here. It is not unusual for certain amino acid or nucleotide sequences to acquire fairly extended and rigid conformations and they may therefore self-order with neighboring sequences into liquid crystalline structures. One wonders therefore if polyflexibility can be effective in phase separation among polymeric sequences in the mixtures of proteins or genes that occur in nature or biotechnological systems.

Conclusions

We conclude that the broad biphasic thermal range observed in liquid crystal polymers results from the "polyflexibility" (persistence length distribution) present in many of these systems. In the specific case of the liquid crystal polymers studied here it is postulated that polyflexibility originates from chemical disorder. Since the relation between polyflexibility and molar mass polydispersity is not universal, broad molecular weight distribution may lead directly to polyflexibility in some systems. Conversely, not all types of chemical disorder will lead to polyflexibility. The conclusions in this paper are based on synthesis and comparative analysis of ordered and disordered isomers and are supported by computer simulation and theory. This simulation allowed us to calculate the theoretical transition temperatures of 10 000 hypothetical "cloned" sequences and generated a curve which is qualitatively similar to the experimentally observed biphasic spread. We believe the concepts studied here could be useful in understanding the behavior of multistructural unit polymers and mixtures of biopolymers with specific chemical sequences.

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Registry No. (A)(B)(C) (copolymer), 102127-78-6.

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Synthesis and Characterization of a Series of Polyimides Derived from 4,4′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]-bis[1,3-isobenzofurandione]

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ABSTRACT: The dianhydride 4,4′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[1,3-isobenzofurandione] (6FDA)[2a] was reacted with a series of diamines, viz., 4,4′-oxybis[benzeneamine] (ODA),[2b] 4,4′-methylenebis[benzeneamine] (MDA),[2c] 4,4′-(2-propylidene)bis[benzeneamine] (IPDA),[2d] 2,7-diaminofluorene (DAF),[2e] 3,3′-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]bis[aniline] (6FmDA),[2f] and 1,5-diaminonaphthalene (NDA),[2g] to form clear, tough, thermally stable polyimides which could be cast into clear, tough films. Characterization of these films by infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, viscometry, density, and birefringence studies is reported.

Introduction

A wide variety of polyimides have been prepared via the general reaction of a diamine with a dianhydride with final imidization effected either thermally or chemically (Figure 1).

These durable materials exhibit high strength and thermal stability,[3] e.g., they retain usable properties at 300 °C for months and even withstand temperatures >500 °C for a few minutes. During the past decade interest in these polymers has increased in response to an increasing variety

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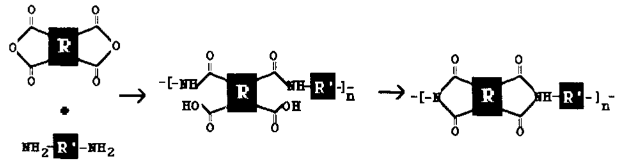

Figure 1. Polyimide formation.

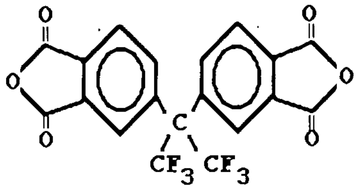

Figure 2. 6FDA.

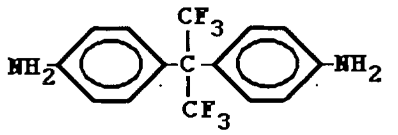

Figure 3. 6FpDA.

of applications in technologies varying from aerospace to medical to microelectronics.[4] Thus, the incorporation of oligomers and polymers as components in adhesives and composites leads to high-strength joints.[5] Further, the electronic interactions between neighboring chains has prompted their use in a variety of electronic devices.[6] But more to our interest has been the observation that the glassy state, which characterizes membranes resulting from these polymers, maximizes, in most cases, the ability of the films to serve as fluid-separation systems.[7] This application, as several others, has often been limited by the insolubility and high glass transition temperature of several polyimides.[8-10]

For the last several years, a major synthetic goal of polyimide chemists has been to prepare aromatic polyimides that can be easily fabricated.[11] This requires that they are (1) soluble in workable solvents or (2) melt processable or (3) can undergo curing with no evolution of volatile materials. One of the most attractive and successful attempts in attaining this goal was the introduction of the perfluoroisopropyl group into the dianhydride by workers at Du Pont and subsequent preparation of polyimides from 6FDA (see Figure 2).[12,13] With this development a new group of soluble or melt-processable materials was obtained.

The increased solubility of the polyimides is presumeably due to the enhanced flexibility of the chain, but the precise mechanism for solubilization has not yet been delineated. In some quarters, it is simply referred to as the "fluorine effect". In any case, inclusion of the hexafluoroisopropylidene group in the amine portion of the molecule also imparts similar solubility (see Figure 3).[14] We thus decided to choose the dianhydride 6FDA as the basis for a series of regularly varying polyimides for future studies of membrane potential.

Structural variations within a polymer alter its inherent membrane productivity as well as its selectivity for different gas pairs in membrane applications. The following diamines were chosen to provide regular structural variation in a series of derivative polymers (see Figure 4). A few have been reported previously. The most often studied appears to have been 6FDA–ODA, with lesser attention given to 6FDA–MDA and 6FDA–NDA.[12,13] Information regarding other polyimides in this study has not been found. A comparative study of these polymers prepared from a consistent synthesis has not been reported.

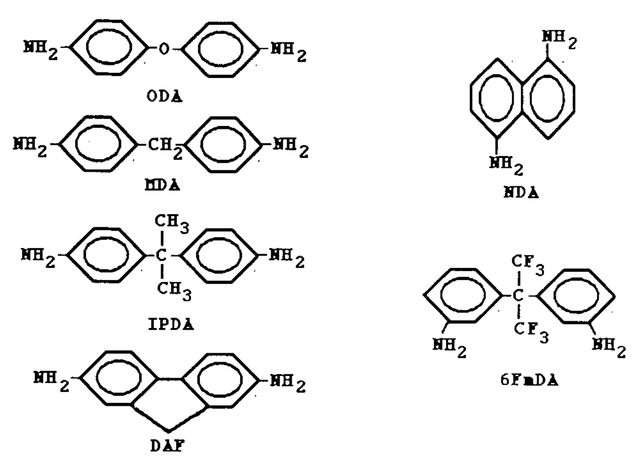

Figure 4. Aromatic diamines.

Several of these diamines were used to provide a regularly varying series of polymers with pyromellitic dianhydride for earlier permeability studies.[15-17]

In this series of diamines, chemical reactivity is not observed to differ markedly. Only slightly differing polar interactions due to the ether linkage in ODA and the fluorines in 6FmDA would be expected. Major effects on permeability due to stereochemical differences in the derived polyimides may be observed. Thus the series of six polyimides, 6FDA–ODA, 6FDA–MDA, 6FDA–IPDA, 6FDA–DAF, 6FDA–NDA, and 6FDA–6FmDA, have been prepared and characterized. Ultimately the relationship between molecular structure of these polyimides and their permeability will be carried out with a variety of gaseous molecules, including several commercially important gas pairs, such as O_2/N_2, H_2/N_2, and CO_2/CH_4.

Experimental Section

1. General Comments. Infrared spectra of polymer films were obtained by using a Perkin-Elmer Model 360 spectrophotometer. Thermal studies were carried out by using a Perkin-Elmer Model 2 differential scanning calorimeter and a Du Pont 9900 thermal analyzer for both DSC and thermogravimetric analysis (TGA). DSC analysis was carried out in a nitrogen atmosphere with 10, 20, and 40 °C/min temperature ramps. T_g's were successfully obtained at the 20 and 40 °C/min regimes.[18] TGA's were obtained under a nitrogen atmosphere by using a 20 °C/min temperature ramp.

Birefringence data were obtained by using a Gaertner polarizing refractometer.

Viscosity measurements were obtained by using standard techniques and Ostwald and Cannon-Fenske viscometers. Solutions of polymer (0.5% in DMAc) were prepared and equilibrated at 30 °C. Size 100 bore viscometers were utilized for experimental determinations.

Densities were determined by means of a standard 70-cm density gradient column by using solutions of calcium nitrate in water. Two columns were prepared, the first with a density gradient from 1.48 to 1.32 g/mL and the second from 1.36 to 1.19 g/mL. The column was calibrated by using standard gradient density beads.

A laminar flow hood designed and built at The University of Texas at Austin was used to prepare dust-free films. Imidization and final solvent removal were effectively carried out by use of 2-μm Nupro filters to remove dust particles.

GPC analyses, carried out by Springborn Laboratories, Enfield, CT, were used to determine molecular weights of the 6FDA polymers in DMF at 35 °C. The polymer, 6FDA–DAF, was originally reported to be insoluble. Solubilization was achieved by 3M Laboratories, St. Paul, MN, by heating to 120 °C for 1/2 h in DMF with 0.5% LiBr. The solution was filtered before GPC was carried out. Difficulty in filtration was indicative of some insolubles in DMF.

2. Starting Materials. The diamines ODA, MDA, DAF, and NDA were purchased from Aldrich Chemical Corporation. The

Table I
Reactions of 6FDA with Diamines

diamine	temp/time[a]	temp/time[b]	yield, %	solubility[c]	M_w,[d] M_n[d]	M_w/M_n
ODA	exotherm, 50 °C/1 h	45–100 °C/30 min, 100 °C/30 min	95%	DMAc, THF, DMF	236 000, 91 900	2.6
MDA	50 °C/2 h	50 °C/1 h, 100 °C/1 h	97%	DMAc, THF, CH_2Cl_2, DMF	302 000, 89 300	3.5
IPDA	54 °C/2 h	55 °C/1.25 h, 99 °C/10 min	97%	DMAc, THF, CH_2Cl_2, DMF	96 700, 33 500	2.9
DAF	52 °C/2.5 h	52 °C/1.25 h red gel	97%	DMAc, DMF	455 000, 170 000	2.7
NDA	69 °C/2 h	50 °C/2 h	95%	DMAc, THF, Ac_2O, CH_2Cl_2, DMF	71 300, 22 100	3.
6FmDA	50–58 °C/3 h	50 °C/1 h, 100 °C/20 min	76%	DMAc, THF, Ac_2O, CH_2Cl_2, DMF	73 000, 25 600	2.8

[a] Time/temperature conditions of the polymerization reaction. [b] Time/temperature conditions of the imidization reaction. [c] Solubility = solubility in listed solvent is 5% minimum, w/w. [d] M_w = weight-average molecular weight; M_n = number-average molecular weight.

Table II
Characteristics of 6FDA Polyimides

diamines[a]	ρ,[b] g/cm³	TGA,[c] °C	T_g, °C	birefringence × 10³	η_{inh} in DMAc
ODA	1.432	480	304	0.145	0.99
MDA	1.400	500	304	0.836	0.57
IPDA	1.352	480	310	0.099	0.51
DAF	1.423	480	394	2.25	1.1
NDA	1.426	525	392	0.0345	0.35
6FmDA	1.433	530[e]	330[f]	0.567	0.28

[a] Diamine component of polyimide. [b] Density of film samples. [c] Temperature at which approximately 5% weight loss occurs. [d] Inherent viscosity measured in dimethylacetamide. [e] On long standing, some samples show marked darkening at temperatures over T_g. [f] After standing, samples show darkening and peaks at 270 and 330 °C.

IPDA was prepared according to the French patent by Grosjean.[19] These diamines were further purified prior to reaction either by vacuum sublimation or short-path distillation. 6FDA and 6FmDA were provided gratis by American Hoechst/Celanese Corporation. They were sublimed under vacuum just prior to reaction.

Reagent grade DMAc from Fischer Chemical Co. was heated at reflux under argon and over calcium hydride for several hours, then distilled onto activated molecular sieves. The acetic anhydride and triethylamine were distilled shortly before use. After purification, all solvents and reactants were stored under argon.

3. Preparation of Polyimides. A 50-mL round-bottom reaction flask fitted with stirrer and gas and vacuum inlets was scrupulously dried and flushed with Argon. The apparatus was charged with equimolar quantities of diamine and dianhydride (5–15 mmol). Immediately, 50 mL of DMAc was added via syringe (under argon) and stirring commenced. A yellow color characteristic of the diamine developed and in some cases an exotherm was observed. After dissolution of the solids and subsidence of any exotherm, the reaction flask was heated to 50–69 °C and held for 1–2 h. The solution was cooled to about 45 °C, and a solution of 40 mmol of acetic anhydride in 40 mmol of triethylamine was added to the reaction mixture. The mixture temperature was raised to 50 °C and held for 1 h, then raised to 100 °C, and held for 20 min. (An unpredictable color change, often red, sometimes appeared at this point. The color dissipated upon workup and did not appear in the final product.) The solution was cooled slightly, then poured into about 1000 mL of methanol. The solid polymer was filtered from the methanol, then placed in a blender with about 500 mL of fresh methanol, and ground to a fine powder. The polymer was vacuum filtered, then dried under vacuum for several hours at 80 °C, and finally dried at 285 °C for 16 h. Details for the reaction of each diamine and pertinent physical properties are given in Table I.

Film Formation. Because of the enhanced solubility of the fluorine-containing polyimides, it was possible to cast them directly from solution. In general, the polymer was dissolved to give a solution with a concentration of about 5–10% polymer. The solution was poured into a ring, positioned on a glass plate so that the liquid uniformly covered the plate surface. A cover with a small vent was placed over the ring. The evaporation rate of the solvent was carefully controlled so that it proceeded slowly and evenly. With low-boiling solvents, the evaporation rate was controlled by means of the vents alone, whereas, with high-boilers, heating was possible. When the solvent has just evaporated, the film must be stripped from the plate and placed in a frame. Final drying was carried out in the vacuum oven for 16 h at 285 °C.

Results and Discussion

As detailed in the Experimental Section, it was possible to form a series of six polyimides from 6FDA and the diamines ODA, MDA, IPDA, DAF, NDA, and 6FmDA. The dianhydride was reacted in 1:1 molar ratio with the chosen diamine with DMAc as a solvent. Reaction proceeded smoothly to the polyamic acid at temperatures near 50 °C. Although thermal imidization can be utilized, we found that dehydration of the polyamic acid was rapidly carried out by using a 1:1 mixture of acetic anhydride/triethylamine. Purification of the polyimide was achieved by washing the polymer well with methanol.

It is important to note that considerable care must be taken when carrying out these reactions on a small scale. A dry, inert atmosphere is needed. Further, DMAc as purchased is seldom suitable for the reaction due to the presence of small amounts of dimethylamine and acetic acid which prevent formation of polymers with high molecular weight.

The 6FDA polyimides were found to be soluble at 5% (w/w) in a variety of solvents, including DMF, THF, chloroform, and acetone as shown in Table I. In some instances, solubilities of 20% (w/w) were achieved. This solubility resulted in the ability to ring-cast the cured polymers on clean glass plates. Strong, durable films were formed. The characteristics of these films are summarized in Table II. The observed solubility of chemically imidized 6FDA–MDA contrasts markedly with the insolubility of thermally imidized 6FDA–MDA reported by T. L. St. Clair et al. in their earlier study of polyimide solubilities.[20]

Polymer Densities. The densities of these fluorinated polyimides are generally greater than those observed for the PMDA analogues, 1.285 (PMDA–IPDA), 1.352 (PMDA–MDA), 1.402 (PMDA–ODA), and 1.432 (PMDA–DAF).[17] (No data are available for the NDA or 6FmDA polymers, whcih did not readily form with PMDA.) The increased density undoubtedly reflects an overall effect due to the fluorine substituents. Thus a parallel increase in density is observed in both series (PMDA versus 6FDA) as one moves from polymers derived from IPDA to MDA to ODA. One might have expected the change of the acid residue from a planar configuration (PMDA) to one containing a tetrahedral center with six fluorine substituents (6FDA) to hinder interchain packing and perhaps result in a decrease in the density. Any such steric effect is apparently overwhelmed by the increased mass of the six fluorine atoms.

Something different can be seen, however, with the two DAF polymers. In contrast to those discussed above, the PMDA–DAF is slightly more dense than the 6FDA analogue 1.432 (PMDA–DAF) versus 1.423 (6FDA–DAF). In addition, while both polymers are more dense than the related IPDA-derived polymers, a much greater density increase is observed for PMDA–DAF. In the case of

PMDA–DAF, where both acid and amine residues are nearly planar, very strong interchain interactions decrease the internal volume markedly. Replacement of PMDA with 6FDA causes severe steric disruption of interchain forces with concomitant increase in internal volume, thus, the increased mass of the fluorine substituents are insufficient to cause the 6FDA polymer to be more dense than its PMDA analogue.

Thermal Studies. Both thermogravimetric analysis (DTA) and differential scanning calorimetry (DSC) were used to examine the samples. Data are summarized in Table II. DTA indicates that appreciable decomposition (5% weight loss) does not occur in any case until past 480 °C. By neither DTA nor DSC do we observe indications of incomplete imidization or appreciable residual solvent, which would be reflected as as weight loss or exotherm prior to decomposition. This is only slightly lower than that observed with PMDA analogues which remained stable to 500 °C or above. This can be compared to the work of Navarre.[21] The nature of the obvious decomposition of long-standing samples of 6FmDA, noted in Table II, has not been further explored but may be related to its lower molecular weight.

Initial DSC studies show lack of any interesting features when scanned with a 10 °C/min ramp in the region 50–500 °C. After such conditioning runs, however, it is possible to confirm T_g's by using 20 and 40 °C/min temperature ramps.[18] These are observed in all cases above 300 °C and in the cases of 6FDA–DAF and 6FDA–NDA approaching 400 °C. The T_g of 6FDA–ODA at 304 °C is quite consistent with observations by other researchers (307 °C,[20] ~310 °C[22]); however, our determined value for the chemically imidized 6FDA–MDA, 304 °C, is somewhat higher than the 290 °C observed for a thermally imidized sample.[20] As with the differing solubility of the 6FDA–MDA from the two separate sources, this may reflect some inherent differences in the samples. Caution in comparisons must be exercised, however, because the characteristics were determined on films which were prepared in a different fashion and by differing methods or measuring conditions in making characterizations.

Infrared Spectroscopy. The infrared absorptions near 3200 (OH) and 3350 cm^{-1} (NH) were used extensively to determine the presence of polyamic acid in the sample and thus incompleteness of the imidization process. Further, the absorption at 3274cm^{-1} was used to detect the presence of residual DMAc in the final products. As a standard, a computer simulation was used to determine at what point these peaks would become visible in the polyimide spectrum. Either DMAc or polyamic acid is easily observed in concentrations as low as 1–2%.

Infrared spectra were taken on thin film samples (0.1 mil) of each polymer. These were generally characteristic and unremarkable. Each polyimide in the series possessed the characteristic imide absorptions in the regions 705–735, 1340–1365, 1715–1725, and 1775–1780/cm^{-1}.[21,23] The spectrum of 6FDA–IPDA polymer is marked by a sharp absorption at 2960 cm^{-1} due to the geminal dimethyl group from the diamine residue. Infrared studies indicate neither the presence of polyamic acid nor DMAc in the final imides.

As independent confirmation, the polyimide was leached with refluxing methanol for several days. Analysis of the methanol solution by gas chromatography indicated that the fully cured polyimide contained less than 0.5% DMAc.

Inherent Viscosities and Molecular Weights. Inherent viscosities of the fluorinated polyimides were determined as a general indication of the suitability of these polymers for film formation. These varied from 0.28 to 1.1 (see Table II). Films that stand up to reasonable manipulation were formed from all polymers.

Molecular weights were determined and can be compared with the inherent viscosities in Table II. A comparison of M_w/M_n shows departure from the theoretical value of 2.0 (ranging from 2.6–3.5). Coupled with the observed solubility of the polymers, this may be indicative of a broad molecular weight distribution. The gel noted in some samples of 6FDA–DAF may result from cross-linking or interchain association. Another potential cause for the deviation from theory is branching, which can occur in the amic acid state. Such a phenomenon would increase M_w more than M_n and therefore create a disparity between these values.

Birefringence Studies. Many polyimide films are commercially sold as biaxially oriented materials. Previous studies involving PMDA diamine polymers with this series of diamines indicated that the aggregation occurring in oriented films caused significant difference in penetration of the film by fluids. In general, films with birefringence values below 1×10^3 have little orientation. Only 6FDA–DAF exceeds this value (see Table II). Thus little or no orientation occurs during the synthesis or casting processes.

Preliminary Permeation Studies. Preliminary data obtained from permeation studies of these polyimides carried out in collaboration with the research group of Dr. William Koros, The University of Texas at Austin, have indicated high permeabilities to fixed gases; e.g., the permeability of hydrogen is roughly four times higher than in celluloseacetate or polysulfone. These latter two polymers are commercially utilized membrane materials for gas separation application. These studies are soon to be completed. Comparisons of these membranes with their PMDA analogues is under way. The role of molecular structure in determining absolute and relative differences between sorption and transport coefficients will be established with several gas pairs.

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Registry No. (ODA)(6FDA) (compolymer), 32240-73-6; (ODA)(6FDA) (SRU), 39940-16-4; (MDA)(6FDA) (compolymer), 57138-86-0; (MDA)(6FDA) (SRU), 57153-28-3; (IPDA)(6FDA) (copolymer), 111367-14-7; (IPDA)(6FDA) (SRU), 11343-89-6; (DAF)(6FDA) (copolymer), 112654-66-7; (DAF)(6FDA) (SRU), 105137-75-5; (NDA)(6FDA) (copolymer), 41274-64-0; (NDA)(6FDA) (SRU), 41040-10-2; (6FmDA)(6FDA) (copolymer), 94289-79-9; (6FmDA)(6FDA) (SRU), 94322-31-3.

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(2) Abbreviations for common names are used in the body of the paper as substitution for the rather complicated systematic nomenclature. The following have been chosen: (a) 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride = 6FDA; (b) 4,4′-oxydianiline = ODA; (c) 4,4′-methylenedianiline = MDA; (d) 2,7-fluorenediamine = DAF; (e) 3,3′-(hexafluoroisopropylidene)-*m*-dianiline = 6FmDA; (f) 1,5-naphthalenediamine = NDA.

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Synthesis and Solid-State Polymerization of a New Diacetylene: 1-(*N*-Carbazolyl)penta-1,3-diyn-5-ol

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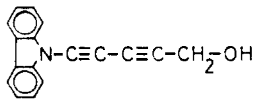
ABSTRACT: A new unsymmetrical diacetylene having a carbazolyl group directly bound to an acetylene moiety, i.e., 1-(*N*-carbazolyl)penta-1,3-diyn-5-ol, was synthesized. This diacetylene can be topochemically polymerized in the solid state and the visible absorption edge of the polymer is expanded to nearly 800 nm, suggesting longer π-conjugation than the so-far-known polydiacetylenes.

Introduction

Solid-state polymerization of diacetylenes is known to give single crystals of conjugated polymers[2] and has attracted attention on their physical properties, such as conductivity,[3-6] optical nonlinearity,[7] and mechanical strength.[8] Especially, it is interesting that the value of the third-order nonlinear optical susceptibility is very large ($\chi^{(3)} = 10^{-9}$–10^{-10} esu) and the response is very fast (less than picosecond order).[9,10] However, since these interesting nonlinear optical properties are due to the π-conjugation, there must be little difference among most polydiacetylenes which have methylene groups next to diacetylene moiety and have the same number of π-electrons per repeating unit, such as poly[2,4-hexadiyne-1,6-diol bis(*p*-toluenesulfonate)] (poly-PTS),[11] poly(1,6-di(*N*-carbazolyl)-2,4-hexadiyne) (poly-DCHD),[12] poly[5,7-dodecadiyne-1,12-diol bis(phenylurethane)] (poly-TCDU),[13] and so on. To achieve higher susceptibility, a polydiacetylene with aromatic substituents directly bound to the main chain, and therefore with increased numbers of π-electrons per repeating unit through the π-conjugation between the main chain and substituents, might be a better candidate. However, few such polydiacetylenes are known: e.g., diphenyldiacetylene and dicarbazolyldiacetylene[14] are not polymerizable, and several substituted diphenyldiacetylens give polymers only in low conversion.[15] In fact, the conductivity of poly(bis(*m*-acetamidophenyl)butadiyne) upon iodine doping was 10^3 order higher than those of polydiacetylenes with methylene groups next to the polymer backbone.[16,4] This is evidence that directly bound aromatic substituents are effective for expanding π-conjugation of poly-DAs.

In polymerizable diacetylene crystals packing parameters, d and ϕ shown in Figure 1, are known to be near 5 Å and 45°, respectively.[17,18] Such a crystal structure is usually observed in diacetylenes which have methylene groups next to diacetylene moiety. In these crystals, bending in the methylene units seems to produce the polymerizable stacks. So, in order to obtain the polydiacetylene with expected conjugation between polymer backbone and side groups, the synthesis of unsymmetrical diacetylenes which have both an aromatic ring and a methylene group directly bound to acetylene moieties seems to be promising.

In this paper, we report the synthesis and the solid-state polymerization of such a new diacetylene: 1-(*N*-carbazolyl)penta-1,3-diyn-5-ol.



Experimental Section

Synthesis of 1-(*N*-Carbazolyl)penta-1,3-diyn-5-ol (CPDO). CPDO was prepared by the Chodkiewicz and Cadiot coupling[19] of *N*-ethynylcarbazole[20] and 1-bromopropargyl alcohol.[21] Catalyst solution was made from Cu(I)Cl (0.1 mmol), 70% aqueous solution

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