Monatshefte für Chemie 109, 1241—1261 (1978)

Monatshefte für Chemie

Higher Aliphatic Aldehyde Polymers, VII[a]: Poly(*n*-Decaldehyde)

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(Received 13 December 1977. Accepted 25 January 1978)

n-Decaldehyde (*DA*) was polymerized to crystalline poly(*n*-decaldehyde) (*PDA*) of reasonable molecular weight in methylcyclohexane (*MCH*) solvent with lithium *tert*-butoxide (*LTB*) as the initiator under carefully controlled temperature conditions. The polyacetal structure of *PDA* was established by IR and PMR spectroscopy as well as by the characteristic degradation of the polymer in the presence of 2,4-dinitrophenylhydrazine. *PDA* had the dual melting behavior typical of aliphatic polyaldehydes with four or more side chain carbon atoms. The DSC scans of crystalline *PDA* in the first, or side chain, transition region showed as many as three endothermic peaks between 45 and 65 °C. The X-ray diffraction pattern of crystalline PDA was similar to that which had been observed for other polyaldehydes but with a larger unit cell. *PDA* was extruded at 53 °C in a capillary rheometer and gave a filament whose X-ray diffraction pattern indicated medium orientation effects.

Polymere höherer aliphatischer Aldehyde, VII: Poly(n-decaldehyd)

Die Polymerization von *n*-Decaldehyd zu einem krystallinen Polymeren von mittlerem Molekulargewicht wurde mit Lithium-*tert*-butylat in Methylcyclohexan unter genauerTemperaturkontrolle durchgeführt. Poly(*n*-decaldehyd) (*PDA*) wurde mittels spektroskopischen Methoden (IR und PMR) charakterisiert, und durch Abbau in der Gegenwart von 2,4-Dinitrophenylhydrazin wurde die Polyacetalstructur des Polymeren bestätigt. *PDA* hat einen „Doppelschmelzpunkt" ähnlich anderer aliphatischer Polyaldehyde mit mehr als vier Kohlenstoffatome in der Seitenkette. *DSC*-Untersuchungen zeigten in der ersten Übergangsregion, der der Seitenkettenkristallisation, daß drei endotherme Spitzen zwischen 45 und 65° beobachtet werden konnten. Das *Debye—Scherrer*-Diagramm des krystallinen *PDA* war ähnlich dem anderer Polyaldehyde, aber mit größerer Einheitszelle. *PDA* wurde bei einer Temperatur von 53 °C in einem Rheometer extrudiert und gab Fasern, deren Röntgenstreuung mittlere Orientierung zeigte.

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[a] Part VI: *J. Starr* and *O. Vogl*, J. Polymer Sci., Polym. Chem. Ed. (in press.).

0026-9247/78/0109/1241/$ 04.20

Introduction

During our work on the polymerization of aliphatic aldehydes with increasing alkyl chain length, it was observed that the polymerization of higher aliphatic aldehydes becomes more difficult as the length of the paraffinic chain increases[1,2]. It became clear that the *n*-alkyl chain more and more dominates the behavior of the aldehyde as the chain length increases. This increasing influence of the alkyl chain is manifested in the polymerization of aliphatic aldehydes in at least two ways: First, the rate of polymerization is decreased and second, the precipitation of the monomer from its solution, which occurs simultaneously and competes with polymerization, becomes an increasingly important problem. As a consequence of these facts, the polymerization of *n*-aliphatic aldehydes higher than *n*-octaldehyde (*OA*) became more difficult and required a programmed temperature profile for the polymerization as competitive crystallization of the monomer became more favorable[3].

Two techniques have been developed[4] for the polymerization of *n*-nonaldehyde (*NA*): In the first type of polymerization a rather narrow temperature range was established where polymerization is in effective competition with crystallization of the monomer and polymerization can be achieved. In the other, more successful technique, initiation was carried out above the polymerization (and crystallization) temperature of the monomer, similar to the methods that were developed[5] for the bulk polymerization of chloral (cryotachensic polymerization). Furthermore, the polymerization of *NA* was only successful if the initial monomer concentration was held in a relatively narrow range.

All higher aliphatic aldehyde polymers were thermally unstable and had to be endcapped[6]. Effective endcapping of polyaldehydes also became more difficult as the polymer side chain length increased. Steric hindrance by the long alkyl group of the monomer at the chain end, rendering difficult the access of the endcapping reagent to the endgroups (secondary hydroxyl or alkoxide group) was considered to be mainly responsible for the poor results in effective endcapping together with the ease of depolymerization. The hydrophobic nature of the side chains possibly also impeded the approach of the endcapping reagent (acetic anhydride) to the chain ends.

With very careful attention to the above characteristics of polymerization and endcapping a moderate yield of 35-40% of polymer (*PNA*) of reasonable molecular weight was obtained[4].

Higher aliphatic polyaldehydes have been found to show the characteristics of side chain crystallization. This behavior has been detected in the case of poly(*n*-valeraldehyde)[7] and has been studied in some detail with poly(*n*-heptaldehyde) (*PHA*)[8]. The crystal structure of *PHA* has been investigated[9, 10] and the polymer was found to crystallize in a manner similar to poly(*n*-butyraldehyde)[11] with small modifications concerning the *c*-axis spacing of the unit cell and the angle of inclination of the side chain with the edges of the unit cell.

Poly(*n*-nonaldehyde) (*PNA*) was also found to be highly crystalline and apparently had a crystal structure similar to that of *PHA*[4]. The transition of the side chain crystallization of *PNA* was composed of more than one endothermic DSC peak. The position of these peaks could be related to their thermal history. When heated to the appropriate temperature, *PNA* could be extruded through an orifice to give an oriented fiber.

It was the purpose of the present work to prepare crystalline *PDA* by anionic polymerization of *DA* and to characterize the polymer by spectroscopic means, to identify the transitions of the polymer and to study the side chain crystallization. It was considered particularly desirable to examine the crystallization behavior of the side chains of *PDA* in relation to the expected decreasing influence of the main chain crystallization on the overall crystallization behavior of *PDA*. Attempts to prepare filaments of *PDA* by extrusion near the side chain melting point was expected to clarify the orientability of the polymer chains of *PDA*.

Experimental Part

n-Decaldehyde (*DA*) was purchased from Aldrich Chemical Co., distilled once (b.p. 44-46 °C/0.6 mm) and stored over molecular sieves 3 A.

Tetrahydronaphthalene (tetralin), methylcyclohexane (*MCH*) and *N*,*N*-di-β-naphthyl-*p*-phenylenediamine were obtained from Eastman Kodak Company. Tetralin and *MCH* were distilled from sodium.

Lithium *tert*-butoxide (*LTB*) was obtained from Ventron Alfa Products and vacuum sublimed (150 °C, 0.1 mm) before use.

IR spectra were recorded with either a Perkin Elmer 727 or 283 spectrometer. PMR spectra were recorded with a Perkin Elmer R-24 or R-32 spectrometer. Thermogravimetric analyses were done on a Perkin Elmer TGS-1 thermobalance and DSC on either a Perkin Elmer DSC-1B or DSC-2 differential scanning calorimeter.

A Mel-Temp capillary melting point apparatus was used for the determination of melting points. X-ray diffraction diagrams were obtained with a Philips diffractometer. Vapor pressure osmometry was done on a Hewlett-Packard HP-302 vapor pressure osmometer. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Massachusetts.

Polymerization of DA in MCH With LTB Initiator

A three-necked 250 ml round-bottomed flask, fitted with a paddle type stirrer, a rectangular adapter, and a reducing adapter closed with a serum stopper and fitted with a Teflon sleeve, served as the polymerization vessel.

The apparatus was assembled hot and cooled under a blanket of dry N_2 through the rectangular adapter.

The flask was then charged with a syringe with *MCH* (60 ml) and 5 ml of a 0.7*M* solution of *LTB* in *MCH* (0.004 mol *LTB*). The stirrer was started and the flask was immersed in a low temperature bath contained in a *Dewar* vessel and maintained at —58 to —60 °C by judicious addition of small quantities of finely divided Dry Ice. After 30 min the flask was charged with *DA* (13 ml, 0.069 mol); the entire charge of aldehyde was delivered in 0.5 min. When the reaction mixture had become a thick white slurry, the temperature of the bath was lowered to —78 °C. After 5 h the stirrer was stopped, the *Dewar* vessel was packed well with Dry Ice and the flask was allowed to sit overnight at —78 °C. The stirrer was restarted and, after 1 h, a chilled mixture of acetic anhydride (85 ml, 0.90 mol) and pyridine (10 ml) was added to the polymerization mixture. After 15 min the cold bath was gradually removed and the reaction mixture was allowed to come to room temperature (30 min). The reaction mixture was poured into 150 ml of chilled (0 °C) acetone, the resulting suspension was suction filtered through a fritted funnel, and the solid product was washed with methanol (20 ml), acetone (2 × 20 ml), a 5:1 mixture of acetone and distilled water, and again with acetone, and dried overnight at 25 mm and room temperature, giving a 10% yield of polymer.

The infrared spectrum of a film (from $CHCl_3$) of the polymer showed strong broad absorptions in the region of 3250 to 2650 cm^{-1}. Two peaks could be identified at 2950 and 2850 cm^{-1} (CH stretch, CH_2). A moderate to weak absorption was found at 1710 cm^{-1} which had a broad shoulder near 1725 cm^{-1} (C=O stretch), moderate to strong absorptions at 1470 cm^{-1} (shoulders near 1460 and 1430 cm^{-1}) and 1370 cm^{-1} (several shoulders) (C—H bending, CH_2, CH_3). A strong, broad absorption band was present from 1190 to 900 cm^{-1} which had resolved shoulders at 1140 and 1120 cm^{-1}, as was an absorption near 730 cm^{-1} having a small shoulder near 740 cm^{-1}.

The PMR spectrum of the polymer ($CDCl_3$) showed a broad absorption in the region of δ = 5.05-4.65 [—O—(R)**CH**—O—] and a single, strong signal at δ = 1.30 [$(\mathbf{CH_2})_x$]. A poorly resolved multiplet, centered near δ = 0.90 ($\mathbf{CH_3}$), was partially overlapped with the strong absorption at δ = 1.30.

The inherent viscosity of a 0.5 g/dl solution of the acetone treated polymer in tetralin (containing 0.5% *N*,*N*′-di-β-naphthyl-*p*-phenylenediamine) at 60 °C was η = 0.84 dl/g.

$(C_{10}H_{20}O)_n$. Calcd. C 76.86, H 12.90. Found C 76.75, H 12.89.

A small sample of the product was transferred to a test tube together with 3 ml of 2,4-dinitrophenylhydrazine reagent and the test tube was agitated in a 60 °C water bath. The polymer particles degraded as they became coated with the yellow solid 2,4-dinitrophenylhydrazone of *DA*. The thick slurry of the hydrazone was filtered and the yellow solid was washed well with ethanol, recrystallized from ethanol, and dried overnight (m.p. 103-105 °C, lit.[12] 104 °C).

Polymerization of DA in MCH With LTB Initiator Using a Controlled Temperature Program

A flamed out 250 ml three-necked round-bottomed flask, fitted with a paddle type stirrer and glass bushing, a Teflon thermometer adapter fitted with a short glass rod, and a ground glass joint fitted with a threeway stopcock, served as the polymerization vessel. The apparatus was assembled hot and cooled under a blanket of dry N_2. The flask was charged with a syringe with

MCH (95 ml) and 6 ml of a 0.59 *M* solution of *LTB* in *MCH* (0.004 mol *LTB*). The stirrer was started and the polymerization vessel was immersed in a —20 °C cold bath contained in a *Dewar* vessel which was equipped with an automatically controlled liquid N_2 cooling coil. After 30 min the flask was charged by a syringe with *DA* (16 ml, 0.085 mol); a clear mixture resulted. After 10 min the bath temperature was decreased to —28 °C in 5 min and then to —35 °C in 5 min. The polymerization mixture was maintained at that temperature for 60 min and the bath temperature was decreased to —40 °C in 5 min and maintained at that temperature for 25 min. The bath temperature was lowered to —50 °C in 10 min, held at that temperature for 10 min, then decreased to —60 °C in 10 min. After 20 min at —60 °C the bath temperature was lowered to —78 °C, the *Dewar* vessel was packed well with Dry Ice and the flask was left overnight at —78 °C.

In an attempt to endcap the polymer, a chilled mixture of acetic anhydride (65 ml, 0.60 mol) and pyridine (10 ml, 0.12 mol) was added. The cold bath was gradually removed and the flask and its contents were allowed to warm to room temperature in 30 min; agitation of the reaction mixture was continued for 1.5 h and the reaction mixture was slowly poured into 200 ml of stirred, chilled (< 50 °C) acetone contained in a 500 ml *Erlenmeyer* flask. A fluffy white solid precipitated and 10 ml of distilled water was added to the suspension which was then warmed to room temperature and filtered through a coarse fritted funnel. The solid product was washed with acetone (2 × 30 ml), a 1 : 1 mixture of acetone water, and again with acetone. The product was then dried for 5 h at room temperature and 0.5 mm (yield 7.1 g, 51 %). For further purification the polymer could be treated with several portions of acetone (in which the polymer is not very soluble) for 2–3 days (75 % recovery). The polymer could also be purified by dissolving it in toluene (1 % solution) and pouring it into chilled acetone (double the amount) to accomplish precipitation. The inherent viscosity (0.5 g/dl in tetralin at 60 °C) was 1.15 dl/g. The IR and PMR spectra of this sample of *PDA* compared very well to those of *PDA* prepared by the previous method.

Extrusion of PDA in a Capillary Rheometer

The acetone treated portion of the *PDA* was extruded at 52 to 53 °C through a tungsten carbide capillary in the capillary rheometer accessory of an Instron Model TTCM. Filaments of two different diameters were extruded using capillaries of different dimensions. The first capillary had a diameter of 0.030″ (0.076 cm) and a length of 1.008″ (2.56 cm). The second capillary had a diameter of 0.050″ (0.127 cm) and a length of 2.008″ (5.10 cm).

The capillary ($d = 0.076$ cm) was fitted to the end of the rheometer barrel and the rheometer was heated to temperature. A portion of the polymer powder was placed into the rheometer barrel and tamped with a brass rod. The plunger [0.375″ (0.95 cm) dia.] was inserted and sample and plunger were allowed to preheat in the rheometer apparatus for 3.5 min. During this period no polymer was extruded under the weight of the plunger. The crosshead was lowered, affixed to the plunger, and polymer was extruded at a crosshead speed of 0.5 cm/min. The force required to maintain the constant crosshead speed was recorded at a chart speed of 10 cm/min and a range setting which corresponded to a 100 kg load for a full scale deflection of the recorder pen. A small, soft, nearly transparent conical shaped plug was recovered from the barrel of the rheometer at the end of the experiment. The plug became harder, waxy and more opaque when it was cooled while soaking in acetone.

The second capillary ($d = 0.127$ cm) was fitted to the end of the rheometer barrel and the remainder of the polymer sample was introduced through the open end of the barrel; the small plug recovered from the first extrusion was introduced last. The extrusion was then repeated with all other conditions exactly as above.

Both extrudates were cut into a number of 10-20 cm pieces and soaked in several fresh portions of acetone at room temperature for 2 h. The 0.076 cm and the 0.127 cm extrudates were stored in the freezer (—15 °C) under fresh acetone in tightly stoppered test tubes. The filaments were rinsed with acetone, blotted dry on filter paper, and dried at room temperature at reduced pressure prior to their use for further studies.

The bulk of the samples of both extrudates was stored in the freezer for ca. 10 days. The filaments were cut with a razor blade to form a molding powder which was washed well with acetone and dried for 5 h at room temperature and reduced pressure and the polymer was then re-extruded at 59 to 60 °C.

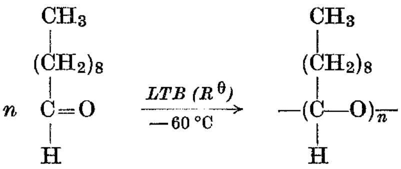
The procedure followed was the same as above. During the preheating stage, some polymer was extruded under the weight of the plunger. An odor of *DA* was noted in the vicinity of the rheometer indicating that a small amount of polymer degradation (to monomer) had occurred. The filament became more brittle and opaque as it cooled. The extrudate was cut into a number of 10-20 cm pieces, soaked with several fresh portions of acetone, and was stored in the freezer (—15 °C) under fresh acetone.

Results and Discussion

Two techniques were successfully used for the preparative synthesis of *PDA* from *DA*. In both cases *MCH* was used as the solvent and *LTB* was the initiator and the polymerization was carried out at low temperature. *PDA* was characterized by IR and PMR spectra, X-ray diffraction patterns, thermal degradation and melting behavior. *PDA* could be extruded at the temperature of the melting of the side chains.

Synthesis and Chemical Characterization of PDA

PDA was prepared by the anionic polymerization of *DA* with *LTB* in *MCH* using two different techniques. In the first technique, which was very similar to the technique which had been successful for the polymerization of *n*-heptaldehyde (*HA*) and *OA*[1], monomer was injected into a mixture of solvent and initiator which was maintained at —58 °C. *DA* is less soluble in *MCH* than *NA* (or, especially, *HA*) and a significant amount of *DA* precipitated immediately when the monomer was injected. However, a sufficient amount of *DA* was soluble or dissolved in the polymerization mixture for polymerization to proceed. (If the initial charging temperature was lower than —58 °C when a similar ratio of monomer to solvent was used, only a trace amount of *PDA* was obtained.) After a period of 30 min the polymerization appeared to be complete and was allowed to proceed overnight at —78 °C. A chilled mixture of acetic anhydride and pyridine was then added to the polymerization mixture to quench the polymerization and also to endcap the polymer. The capping reaction was allowed to proceed for 1 h at room temperature. *PDA* was isolated by pouring the reaction mixture into chilled methanol and filtering the resulting suspension. *PDA* was isolated in 10% yield with an inherent viscosity of 0.84 dl/g.



$$n\ \underset{\mathrm{H}}{\overset{\mathrm{CH_3(CH_2)_8}}{\mathrm{C{=}O}}}\ \xrightarrow[-60\,^\circ\mathrm{C}]{LTB\,(R^{\ominus})}\ -\!(\underset{\mathrm{H}}{\overset{\mathrm{CH_3(CH_2)_8}}{\mathrm{C}}}-\mathrm{O})_{\overline{n}}-$$

In the second procedure, monomer was added to a mixture of solvent and initiator at —20 °C; a homogeneous mixture was formed. The temperature of the polymerization mixture was then brought to —78 °C in 1.5 h by decreasing the temperature at a rate of about 1 °C/min; the decrease was slower between —45 °C and —60 °C. After the polymerization mixture was allowed to sit overnight at —78 °C a chilled mixture of acetic anhydride and pyridine was added to quench the polymerization and endcap the polymer. The reaction was allowed to proceed for several hours at room temperature. *PDA* with an inherent viscosity of 1.15 dl/g was isolated in 53% yield by pouring the reaction mixture into cold acetone. When the reaction mixtures were poured into either methanol or acetone, *PDA* was obtained with much greater ease than when isolation by direct filtration of the reaction mixture was attempted.

DA had previously resisted all attempts for its anionic polymerization by conventional aldehyde polymerization techniques. The crystallization of the monomer in the reaction mixture at the polymerization temperature had been cited as the most likely general reason for the failure of these reported polymerization attempts[2]. However, with the proper choice of solvent and monomer concentration and with the proper control of temperature, a favorable ratio of the rate of polymerization to the rate of monomer crystallization could be achieved and *PDA* was obtained. It was also observed that *PDA* was quite unstable under the conditions traditionally used for the endcapping of polyaldehydes and excessive heating of the endcapping reaction above room temperature drastically reduced polymer yield.

In both procedures the endcapping reaction was carried out only for a few hours. Even when the endcapping reaction was carried out under these mild conditions, the polymers were sufficiently stabilized to be isolated at room temperature and stored for several days. The extent of endcapping reaction was not quantitatively determined but does not appear to be complete by this room temperature treatment, however, carbonyl absorption from the acetate end groups was found in the infrared spectrum of the polymer. When the treatment of the polymer with the Ac_2O mixture was carried out at room temperature for 1 h (first procedure), the resulting polymer deteriorated more rapidly than if the reaction was carried out for a longer period of time (second procedure). *PDA* obtained by the second procedure, in which the temperature history was more carefully controlled and the endcapping reaction was of longer duration, was used for the characterization of *PDA* by thermal and other techniques.

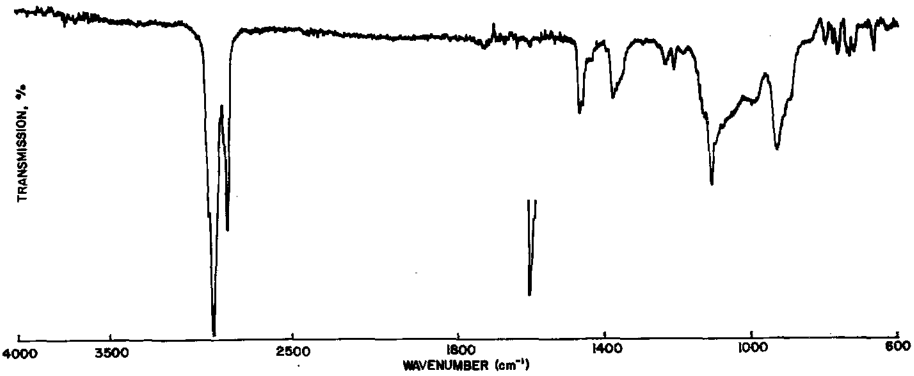


Fig. 1. Infrared spectrum ($CHCl_3$ solution) of *PDA*

The solubility characteristics of *PDA* were similar to those of *PNA* but *PDA* could also be dissolved in toluene and precipitated with acetone.

PDA was degraded by the acidified 2,4-dinitrophenylhydrazine reagent; the hydrazone melted at 103 to 105 °C

The infrared spectrum of *PDA* (Fig. 1) indicated that the polymer indeed had the expected polyacetal structure. Only minor differences were observed between the infrared spectrum of *PDA* and that of *PNA*.

The PMR (90 MHz) spectrum of the polymer was consistent with the structure of the polymer (Fig. 2) and similar to that of *PNA*. It was necessary to use a solution of low polymer concentration for the PMR experiments because *PDA* forms highly viscous solutions in $CDCl_3$. As expected, the apparent relative intensity of the absorption in the region of $\delta = 4.5$—5.0 ppm was broad and weaker in the case of *PDA* because of the relatively lower concentration of acetal protons. The PMA spectrum of *PDA* was very similar to that of *DA* cyclic trimer[13] and indicated again the similarity in chemical structure between the two species.

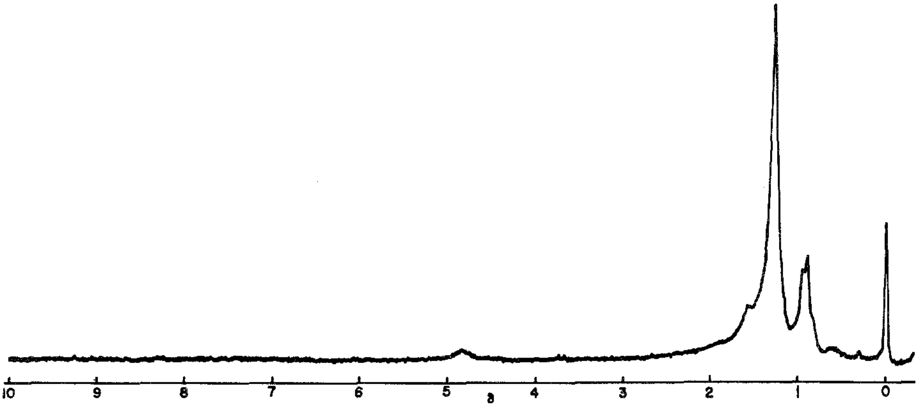


Fig. 2. PMR spectrum (90 MHz) of *PDA*

Thermal Stability of the Polymer

As in the case of *PNA*, the temperatures of onset of weight loss and the temperature of some arbitrary (5 %) weight loss were found to be the most consistent and reproducible criteria for comparing the thermal stabilities of samples of *PDA*. Acetone treated *PDA* had a temperature of onset of weight loss of 95 °C and a temperature of 5 % weight loss of 105 °C. These temperatures were slightly higher than the corresponding temperatures of similarly treated *PNA*. This behavior could have been due to a slightly higher thermal stability of *PDA* but may simply have reflected the higher boiling point of the thermal degradation products of *PDA*. When *PDA* was reprecipitated from toluene the temperatures of onset of weight loss and 5 % weight loss were found to increase indicating a higher thermal stability for the reprecipitated material. This phenomenon, which was also encountered in the case of *PNA*, was believed to be the result of a decrease in level of impurities in the polymer and/or the removal of less stable fractions.

The relative stabilities of samples of *PDA* could also be assessed by visually comparing the shelf life of the samples. *PDA* which was treated with acetic anhydride for only 1 h at room temperature completely decomposed to monomer (identified as its 2,4-dinitrophenylhydrazone) within 2 days at room temperature in the dark. A period of 4 to 5 days was required for complete decomposition of *PDA* which was treated with acetic anhydride for a longer time. When samples of *PDA* were stored in open containers at room temperature and exposed to ambient laboratory light, all samples deteriorated at a greater rate.

X-Ray Diffraction Pattern of PDA Powders

The X-ray diffraction diagram of a powdered sample of toluene reprecipitated *PDA* with the calculated spacings and relative intensities is listed in Table 1. The X-ray diffraction diagram indicated that, as in the case of *PNA*, the overall crystallinity of toluene reprecipitated polymer was lower than in other samples. In this case *PDA* showed the strongest diffractions at smaller angles, in analogy to *PNA* which had been dissolved in toluene and reprecipitated by acetone. Other crystalline comb-like polymers, where only the paraffinic side chains participate in the crystal lattice, show significant small angle X-ray reflections which are related to planes which contain the side chain ends and which are perpendicular to the long axis of the side chains[14, 15]. The X-ray diffraction of *PDA* will be discussed further in relation to extruded samples of *PDA*.

Table 1. *X-ray diffraction pattern of PDA*[a]

Reflection No.	Relative Intensity	d (Å)	Comments
1	ms	24.28	
2	s	14.41	diffuse
3	m	7.15	diffuse halo
4	m	4.87	
5	m	4.49	diffuse
6	—	—	may be part of diffuse refl. 5

[a] Sample reprecipitated from toluene and ground at —50 °C; exposure time, 8 h; sample-to-film distance, 114 mm.

Investigation of the Melting Behavior of PDA by DSC

The melting behavior of *PDA* was investigated by DSC but was augmented by investigation of the polymer transitions by optical microscopy. In some cases observations made during the DSC

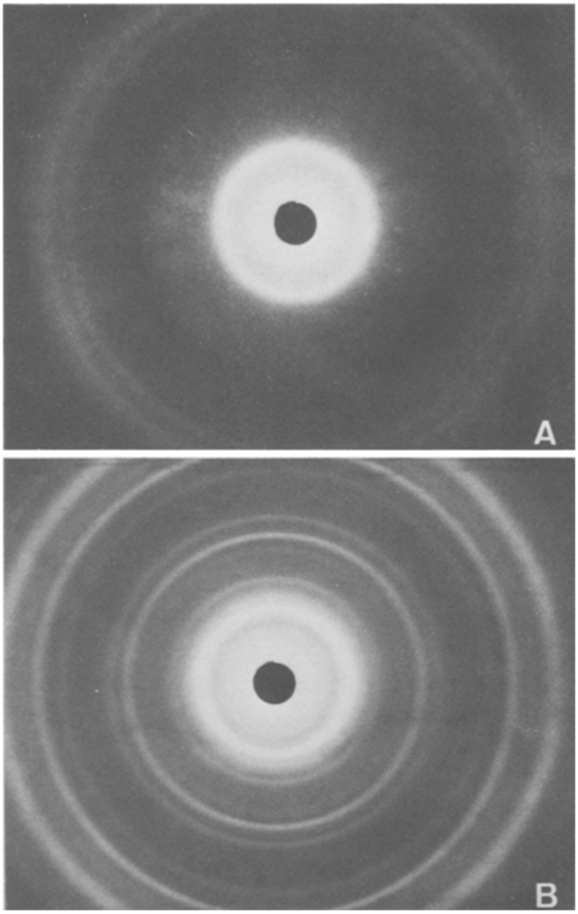


Fig. 3. X-ray diffraction pattern of *PDA*; *A* cold rolled, *B* extruded

experiments could be correlated with the polymer stability. Polymer degradation during the DSC measurements was a still more significant factor in the investigation of the melting behavior of *PDA* than even in the case of less completely stabilized *PNA*[4]. Normally, peak temperatures of maximum degradation rates were found to give the most convenient and reproducible description of the endothermic transitions, particularly in the first transition region.

As in other higher aliphatic polyaldehydes, two transition regions were observed when the melting behavior of *PDA* was investigated by

DSC[1]. The first transition for *PDA* occurred over the range from 40 to 65 °C, and consisted of a series of endothermic peaks or a single peak with shoulders. The transition in this temperature region was also confirmed by optical microscopy. Significant changes in the way polarized light was transmitted through a sample of *PDA* were observed in the region of 56—65 °C; however, the sample maintained a significant degree of structural integrity at these temperatures. A second transition was observed in the region of 110—130 °C by DSC for samples of *PDA*. When a sample of *PDA* was observed between crossed polars, the sample transformed to a viscous, optically isotropic fluid between 95-110 °C. Significant degradation commenced at temperatures near 90 °C and thus, polymer degradation effectively interferred with the accurate observation of the second transition. As a result, the second transition and degradation endotherms were usually poorly resolved and the second transition was, at best, observed as an inflection on the low temperature side of the decomposition endotherm. In rare cases a more clearly resolved shoulder, not observed in TGA measurements, was recorded on the decomposition peak. The significant overlapping of degradation with the second transition of *PDA* was also indicated in hot stage optical microscopy experiments.

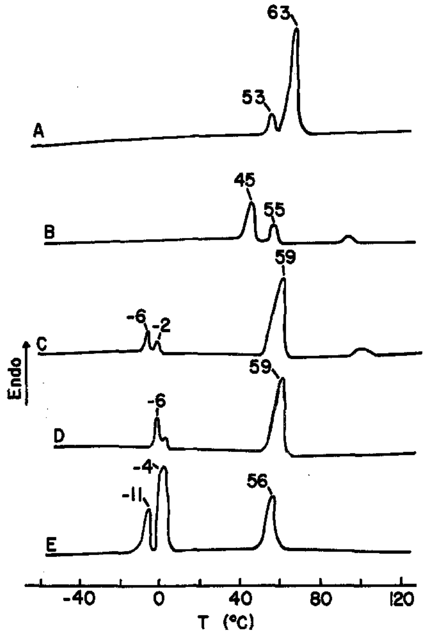


Fig. 4. DSC scans of *PDA* (heating rate 20 °C/min)

Table 2. *DSC scans of PDA*[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (°C)	ΔH First Transition (cal/g)	Second Transition[c] Temperature (°C)
A	Acetone treated polymer, first scan to 90 °C	47; 58	11.2	—
B	After first scan (A) quenched to —30 °C and rescanned to 90 °C	(50)[d]; 60	9.3	—
C	After second scan (B) quenched to 57 °C and annealed 10 min, quenched and rescanned	(54)[d]; 58	8.2[e]	125
D	Polymer reprecipitated from toluene, first scanned to 80 °C	50	5.9	—
E	After first scan (D) quenched and rescanned	35	8.1	130

[a] Data of DSC scans of Fig. 4. [b] Same as in Fig. 4. [c] Estimated. [d] Shoulder. [e] Low temperature transitions recorded, peaks at —9 and —5 °C. Area of low temperature transition corresponded to 4.9 cal/g based on initial sample weight.

Typical DSC scans of different samples of *PDA* are reproduced in Fig. 4, but only the first transition region is shown. Pertinent data relating to the thermograms of Fig. 4 are collected in Table 2. In some cases, transitions were observed in samples of *PDA* at lower temperatures.

Depending on the thermal history of the samples the first transition of *PDA* showed as two overlapping endothermic peaks or a single peak with very noticeable shoulders. A transition enthalpy of 10 to 11 cal/g was calculated for the first transition of a *PDA* sample washed with acetone. The effect of sample history was particularly evident in a sample of *PDA* which had been reprecipitated from a toluene solution. The enthalpy associated with the first transition of this reprecipitated *PDA* was notably lower than the enthalpy associated with the first transition of the native material (5 cal/g vs. 10 cal/g). The enthalpy was found to increase when a sample of reprecipitated *PDA* was scanned through the first transition a second time; this indicated an annealing or improved crystallization. This behavior of *PDA* was very similar to that of *PNA* and the quenching effect of reprecipitation from toluene was clearly demonstrated. The lowering of first transition peak temperatures observed when *PDA* was reprecipitated was less than that observed in the case of *PNA*. Furthermore when a sample of reprecipitated *PDA* was scanned through the first transition region, quenched, then rescanned, the peak temperatures in the second scan were more than 15 °C lower although the enthalpy associated with the first transition was nearly 30% higher than in the initial scan. Reprecipitated *PDA* was less thermally stable than reprecipitated *PNA* and, hence, could not be as extensively annealed. However, a trend to increased transition enthalpy with thermal treatment was seen for reprecipitated *PDA* which, taken with other factors, indicated that the reprecipitation from toluene produced a history in the samples of both *PDA* and *PNA* which had the effect of thermal quenching.

The effects of crystallization of side chains in reprecipitated *PDA* upon heating a sample of the polymer were also seen by optical microscopy as in the case of *PNA*. The initially high optical extinction of reprecipitated *PDA* decreased when the sample was heated to 55 °C and the increased transmission persisted when the sample was cooled.

A transition was frequently seen below room temperatures in DSC scans of samples of *PDA*; this was believed to be the result of the presence of monomer in the polymer. These low temperature peaks were usually observed in samples of *PDA* which had been heated or aged in the DSC sample pans. Again, *PDA* was found to be less stable than *PNA* and the peaks appeared when the samples were treated under less drastic conditions. Typically, this low temperature transition was also observed as a multiple peaked endothermic transition.

When low temperature peaks were observed, then the details of the first transition of *PDA* were altered in a more complex way. If a very small (ca. 3 cal/g polymer sample), multiple peaked, low temperature transition was recorded in the DSC scan of a sample, the enthalpy associated with the first transition endotherm was usually lower than for scans which showed no low temperature peaks. When the low temperature peaks were relatively small (corresponding to up to 8 cal/g polymer sample), the relative areas of both low temperature peaks were comparable and enthalpies of up to 6 cal/g were observed for the first transition. As the total area of the low temperature transitions increased, the peaks gradually coalesced to a single peak at —4 to —5 °C and the first transition peak areas became drastically smaller.

When *PDA* samples were treated in the calorimeter under conditions which were expected to enhance polymer degradation, then the appearance of the low temperature transitions in DSC scans of the "polymer" sample gradually approached that of the DSC scans recorded for monomeric *DA* in independent experiments. If a significant low temperature transition was observed, then the transitions normally observed above 90 °C (including polymer degradation) were suppressed or totally absent.

The best explanation of the low temperature peaks was that polymer and monomer were capable of cocrystallization involving the side chains of the polymer and the alkyl group of the monomer. Such a phenomenon strongly influenced the side chain crystallization in *PDA*; the lower temperature peak of the low temperature region represented the fusion of cocrystalline regions which were relatively rich in monomer whereas the higher temperature peak of the low temperature transition was believed to represent the fusion of "free" monomer. The merging of the two transitions of the low temperature regions seemed reasonable when more monomer was present in the degraded polymer. The suppression of the higher temperature transitions (main chain melting and degradation) when significant low temperature transitions were observed seemed to indicate that significant degradation had already occurred and that the monomer dissolved in the polymer promoted the degradation of remaining polymer in the DSC, causing a broadening of the transitions of remaining polymer.

Extrusion of PDA and Characterization of the Extrudate

At room temperature *PDA* was waxy and brittle but at temperatures in the range of the first transition region, *PDA* became tough and could be extruded to a coherent filament. *PDA* was extruded at 53 °C through capillaries with different *L*/*D* ratios. When the initial extrudates were reextruded at 60 °C, X-ray investigations indicated that, contrary to the case of *PNA* extrusion, significant orientation was not achieved in the *PDA* extrusion process.

PDA powder was extruded at 53 °C through two different capillaries with *L*/*D* values of 34 and 40 respectively. An average value of the apparent viscosity of 1.4×10^4 poise was calculated when the capillary with an aspect ratio 34 was used; an average value of 5.8×10^4 poise was calculated for a *L*/*D* ratio of 40. These values were calculated by using the value of the force indicated by the best horizontal line which could be drawn through the force traces.

Both extrudates obtained at 53 °C were pelletized, combined, and reextruded at 60 °C through a capillary with aspect ratio of 34. The extrudate appeared soft and rubbery and could easily support its own weight. The filaments obtained from each extrusion were easily coiled while warm, but became "set" and brittle when cooled. Ideal conditions of steady state capillary flow were not approached in these extrusion experiments because the force traces were not very regular.

The thermal stability of *PDA* extruded at 53 °C was examined by TGA; the temperature of onset of weight loss and temperature of 5% weight loss (110 and 115 °C respectively) for the acetone washed and dried extrudate were slightly higher than for the original powder. This observation was thought to be the result of the removal of a highly unstable fraction through thermal degradation of polymer during the extrusion. Degradation of *PDA* during DSC measurements on powder samples was strongly suspected. For this reason it was attempted to investigate the thermal stability of *PDA* extrudate under conditions simulating more severe, average conditions to which samples were subjected during the DSC experiments.

Known weights of *PDA* extruded at 53 °C were placed into tared DSC sample pans which were then sealed. The sample pans were then heated under an atmosphere of N_2 in a beaker fixed in a water bath which was held at 72 °C. Sample pans were removed at various time intervals, opened, and their contents extracted with acetone. After 10 min 60% acetone insoluble material remained, but after 25 min only 20% acetone insoluble material remained. On the basis of these observations it was confirmed that significant polymer degradation occurred during DSC measurements of the extrudates.

The extrusion process affected the first transition melting behavior of *PDA* in a peculiar and unique way. The peak temperatures of the extruded material were higher than those of the original powder and the higher temperature peak of the first transition was clearly dominant. The enthalpy associated with the first transition was always greater for the extruded samples than for samples of the original powder. Furthermore, the "melt" enthalpy associated with the first transition of extruded *PDA* was always less when a sample of the extrudate was heated through the first transition, cooled, and then rescanned. This behavior was quite contrary to what had been observed for *PNA*[4] and, particularly, *PHA*[10].

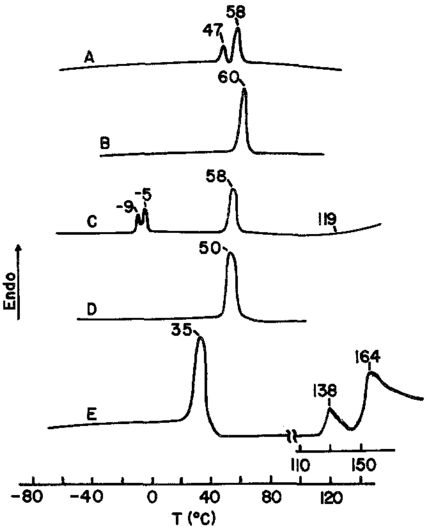


Fig. 5. DSC scans of extruded *PDA* (heating rate 20 °C/min)

The second transition of *PDA* was less readily observed in samples extruded at 53 °C, particularly if even a small amount of monomer was present in the sample. The polymer degradation endotherm was sometimes even missing in extruded *PDA*. The second transition of extruded *PDA* was more easily observed by optical microscopy and occurred at lower temperatures and over a broader temperature range (15 °C) than in the case of the original *PDA* powder. The influence of polymer degradation and polymer crystallization were thought to account for the suppression of higher temperature endotherms of *PDA*.

Typical DSC scans recorded for *PDA* extruded at 53 °C through a capillary having $L/D = 34$ are reproduced in Fig. 5 and are described in Table 3. The thermograms of such *PDA* samples were identical as far as peak shapes and transition enthalpies were concerned with polymer samples extruded with $L/D = 40$ capillary. The melting of the *PDA*

Table 3. *DSC scans of PDA extruded at 53 °C*[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (°C)	ΔH First Transition (cal/g)
A	First scan to 80 °C	53[c]; 63	15.5
B	After first scan to 80 °C (A) quenched and rescanned	45; 55[c]	12.0
C[d]	Heated to 80 °C, quenched to 52 °C and annealed 7 min, quenched	59	7.4
D[e]	Heated to 80 °C, quenched to 52 °C and annealed 12 min, quenched	59	7.4
E[f]	Heated to 85 °C, quenched to 52 °C and annealed 18 min, quenched	56	5.9

[a] Data of DSC scan of Fig. 5. Capillary $L/D = 34$. [b] Same as in Fig. 5. [c] Shoulder. [d] Low temperature transition recorded, peaks at —6 and —2 °C. [e] Low temperature transition recorded, broad peak —6 °C. [f] Low temperature transition recorded, peak at —4 °C, shoulder at —11 °C. Total area corresponded to 18.1 cal/g based on initial sample weight.

extrudate was not found to be significantly dependent upon heating rate. However, endothermic shifts in the region of the second transition of *PDA* were more obvious at higher heating rates. The enthalpy associated with the first transition endotherms are always the same as the enthalpy associated with the first transition exotherms when heating or cooling rates of 20 °C/min or 40 °C/min were used. Polymer degradation interferred at lower heating rates, but precision was sacrificed at higher heating rates.

The major effect of extrusion of *PDA* at temperatures within the first transition region appeared to be an annealing of the first transition. Peak temperatures and transition enthalpies were invariably higher for extruded *PDA* as compared to the initial powder. X-ray investigations indicated, however, that orientation of *PDA* during the extrusion was not significant.

The enhancement of the first transition of *PDA* induced by the extrusion process was even more evident in the thermograms of the extrudate obtained by reextrusion of the original extrudates at 60 °C through a capillary having $L/D = 34$. The peak shapes of this extrudate were identical to those of the 53 °C extrudate, however, peak temperatures were 5–6° higher and heats of fusion of 17–18 cal/g were observed (Fig. 6). Transitions above the first transition were more clearly evident in thermograms of *PDA* extruded at 60 °C, the exact reason for this is not known.

X-ray diffraction patterns of *PDA* extruded at 53 and 60 °C indicated that the orientation of polymer by this extrusion was much less significant than had been observed in the case of *PNA*[4]. This situation severely hindered the efforts toward elucidating the crystal structure of *PDA*. However, the number and intensity of reflections observed in the diffraction diagrams of extruded *PDA* strongly suggested that *PDA* still crystallized in a manner which incorporated both main chains and side chains in the unit cell (see Fig. 3, B).

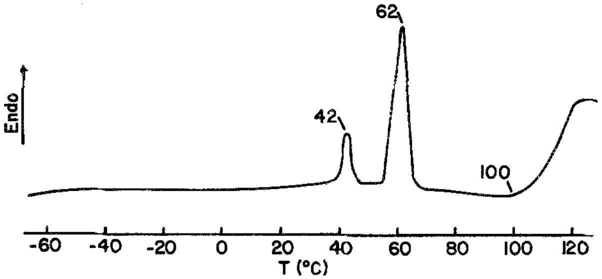


Fig. 6. DSC scan of *PDA* reextruded at 60 °C (heating rate 20 °C/min)

In comb-like polymers where polymer crystallinity arises solely from the packing of the side chains only a few reflections are generally observed at larger angles, the strongest of which corresponds to a spacing near 4.2 Å. In such polymers two reflections are generally observed at smaller angles which correspond to the type of layer packing of the side chains[16].

Numerous attempts were made to prepare oriented samples of *PDA* by mechanical treatment, such as rolling (Fig. 3, A) and cold drawing, of *PDA* extrudate but only brittle material was obtained from the mechanical treatment. X-ray and DSC investigations indicated that no change in the orientation or in the melting behavior of *PDA* was achieved by additional mechanical treatment.

Melting Behavior and Crystal Structure of PDA

Two transition regions were identified for *PDA*. The first transition of *PDA* (40 to 65 °C) represented a change in the packing of the aliphatic side chains whereas the second transition region (110 to 130°) reflected the true melting of the polymer involving the final collapse of a crystal lattice which incorporated the main chains. X-ray investigations also indicated that *PDA* was capable of existing in a crystalline form in which both main chains and side chains participate in the unit cell. As mentioned before, the number and intensity of wide angle reflections were too significant to assume that crystallization of *PDA* involved only the alkyl side chains. The pattern of the X-ray diffraction of *PDA*, particularly for the extruded samples, suggested that the unit cell which incorporated both main and side chains was probably tetragonal, as in the case of *PNA* and *PHA*, or perhaps a slight modification (orthorhombic) of this structure. Some of the reflections observed in the X-ray diffraction diagrams of *PDA*, particularly the reflection which corresponded to a spacing of 4.2 Å, were undoubtedly due to the crystallization of the side chains. IR spectrum of a *PDA* film cast from $CHCl_3$ suggested that the side chains of *PDA* were hexagonally packed as indicated from the IR absorption peak near 720 cm^{-1} (ref. [17,18]). An attempt was made to measure directly the infrared spectrum of extruded *PDA* in order to compare this IR spectrum with that of a solvent cast film, but the IR spectra were not conclusive.

PDA was quite unique in comparison to other comb-like polyaldehydes of shorter aliphatic side chain lengths, especially as far as the influence of the extrusion process on the polymer melting behavior in the first transition region was concerned, indicating a greater influence of the aliphatic side chains.

A significant change in polymer properties over a narrow range of side chain lengths had been observed in the case of comb-like poly(α-olefins)[19,20]. Thus, the fact that *PDA* behaved in a peculiar manner as compared to *PHA* was not alarming, particularly since a trend to increasing influence of the side chain on polymer properties had already been observed in the case of *PNA*. Extrusion of *PDA* appeared to have an annealing effect on the side chain crystallization, and in first approximation, the thermal annealing effects appeared to be more significant then mechanical work effects. At extrusion temperatures the orientation induced by the mechanical effects may have induced a "crystallization" of the side chains before a significant orientation of main chains was induced. As a consequence, independent crystallization of the side chains interferred with the crystallization of the main chains. It was thought possible that if higher temperatures were used during extrusion then a more favorable relative rate of main chain crystallization might have resulted in a more oriented sample of *PDA*. However, even when *PDA* was extruded at 60 °C, a temperature several degrees above the highest peak temperature observed for powdered *PDA*, the annealing effect of the extrusion process, was still clearly evident. However, it must be remembered that, under the pressure of this experiment, the melting point, even the side chains melting point of this thermomechanically treated sample, might have been increased by 10 to 30 °C.

Acknowledgements

This work was supported under Thrust II of the Materials Research Laboratory, National Science Foundation Grant.

We are also indebted to *L. S. Corley* for his efforts in the preparation of this manuscript. We would like to acknowledge the assistance of *W. G. Perkins* in the extrusion experiments.

The paper was written while one of us (*O. V.*) was on sabbatical leave from the University of Massachusetts, and a recipient of the Award of the Alexander von Humboldt Stiftung and visiting professor at the Institute of Organic Chemistry, Free University, Berlin.

References

[1] *I. Negulescu* and *O. Vogl*, J. Polym. Sci. **A1—14**, 1995 (1976).

[2] *O. Vogl*, J. Polym. Sci. **A2**, 4607 (1964).

[3] *J. Starr* and *O. Vogl*, Abstracts, 7th. N.E.R.M., Amer. Chem. Soc., Rochester, N. Y., 311 (1976).

[4] *J. Starr*, Ph. D. thesis, University of Massachusetts, 1977.

[5] *O. Vogl*, *H. C. Miller*, and *W. H. Sharkey*, Macromolecules **5**, 658 (1972).

[6] *O. Vogl*, Chem. and Ind. **1961**, 748.

[7] *O. Vogl*, J. Polym. Sci. **A2**, 4621 (1964).

[8] *I. Negulescu* and *O. Vogl*, J. Polym. Sci. **A1—14**, 2415 (1976).

[9] *I. W. Bassi*, Rend. Ist. Lombardo Sci. Pt. 1 **94A**, 579 (1960).

[10] *J. Wood*, *I. Negulescu*, and *O. Vogl*, J. Macromol. Sci. (Chem.) **A11** (**1**), 171 (1977).

[11] *G. Natta*, *P. Corradini*, and *I. W. Bassi*, J. Polym. Sci. **51**, 505 (1961).

[12] Handbook of Tables for Organic Compound Identification (*Z. Rapport*, ed.). Cleveland, Ohio: Chemical Rubber Company. 1967.

[13] *J. Starr* and *O. Vogl*, J. Macromol. Sci. (Chem.), in press.

[14] *V. P. Shibaev*, *B. S. Petrukin*, *Yu. A. Zubov*, *N. A. Plate*, and *V. A. Kargin*, Vysokomol. Soedin. **10A**, 216 (1968).

[15] *N. A. Plate*, *V. P. Shibaev*, *B. S. Petrukin*, *Yu. A. Zubov*, and *V. A. Kargin*, J. Polym. Sci. **A1—9**, 2291 (1971).

[16] *N. A. Plate* and *V. P. Shibaev*, J. Polym. Sci., Macromol. Rev. **8**, 117 (1974).

[17] *D. Chapman*, Chem. Rev. **62**, 433 (1962).

[18] *D. Chapman*, J. Chem. Soc. **1957**, 4489.

[19] *A. Turner-Jones*, Makromol. Chem. **71**, 1 (1964).

[20] *G. Trafara*, *K. Reimer*, *K. Blum*, and *D. Hummel*, Makromol. Chem. **177**, 1089 (1976).