Synthesis and Thermal Properties of Poly(ethynyldimethylsilane-co-dimethylsiloxanes)

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Homologs of ethynyldimethylsilanes $-C\equiv C-[-Si(CH_3)_2-C\equiv C-]_m$ with various
unit lengths were synthesized by reacting di-Grignard ethyne with 1,4-dichlorodimethyl-
silane in tetrahydrofuran (THF). Poly(ethynyldimethylsilane-co-siloxane)s, [PESSs],
$-[-\{C\equiv C- Si(CH_3)_2-\}_{m+1}-O-Si(CH_3)_2-]_x-$ were synthesized by conden-
sation polymerization of ethynyldimethylsilane and 1,3-dichlorotetramethyldisiloxane
with high yields. They were identified by IR and NMR spectra and their molecular
masses and molecular mass distributions measured by GPC. Thermal properties of the
copolymers were determined by DSC and TGA; the glass transition temperatures go
symbatically with the length of the ethynyldimethylsilane unit. In the case of $m = 5$ the
polymer exhibits peculiar behavior: the usual strong melting peak is absent, but there is
a transition which appears to be liquid crystalline. All polymers synthesized exhibit
good thermal stabilities.

Keywords: Poly(ethynyldimethylsilanes); dimethylsiloxanes; copolymers; synthesis;
structure; properties

1. INTRODUCTION

Since polysilanes were obtained by Kipping and Sands [1,2], the
linear and cyclic silanes have been studied by a number of researchers,
in particular by Gilman [3], Kumada [4] and Hennge [5]. Silicone
polymers have been used as thermoplastics, rubbers and in making

lubricants [6 8]. Polymerization of acetylene reported originally by Nieuwland and coworkers [9] became a favorite way to obtain electrically conductive materials by taking advantage of the overlap of π electrons. However, intended industrial applications turned out to be limited in scope because of unstable bonds in the polymer main chain. Luneva and her coworkers reported [10, 11] the synthesis of polysilylethyne from di-Grignard ethyne and dichloroalkylsilane. This is a sensible approach since di-Grignard ethyne can be obtained more easily than mono-Grignard ethyne. However, the polysilyl ethyne used by Luneva and collaborators involves problems related to the reproducibility and yields, as well as the molecular weights; they obtain the weight-average molecular mass $M_w \approx 3,000$ only. Iwara *et al.* [8] reported a synthesis of poly (ethynyldisilane) with BuLi instead of with the Grignard reagents. In that case as well industrial applications seem remote because of the low molecular mass of the poly(ethynyldisilane) obtained.

It is well known that polymer liquid crystals (PLCs) contain typically mesogenic LC groups (such as the phenyl groups) and also flexible sequences (consisting for instance of the methylene groups) in one chain. The two kinds of units can be put together in a variety of ways, resulting in several classes of structures, each class with distinct properties [12–14]. Popular among this variety of PLCs — because of potential applications - are fully aromatic polyesters. However, the popularity is not entirely deserved; processing is quite difficult because of high melting temperatures. Clearly, we need to look for ways of lowering the melting temperature T_m. One of these is the development of PLCs based on using the siloxane group as the flexible unit [15–18].

In this work we have synthesized poly(ethynyldimethylsilane-co-dimethylsiloxanes) [PESSs] which contain both ethynyl and siloxyl groups, providing respectively rigid and flexible sequences in the main polymer chain. Thus, these are longitudinal PLCs [12–14]. The ethynyldimethylsilanes —$C \equiv C$— [—Si(CH$_3$)$_2$—$C \equiv C$—]$_m$—, called in this work A_m, of various unit length $m = 1, 2, 3$ and 4, were synthesized from di-Grignard ethyne and dichloromethylsilane. Then PESSs were synthesized by condensation of one of the A_ms with 1,3-dichlorotetramethyldisiloxane (D). Their thermal properties were also studied, exploring potential liquid crystallinity of these polymers.
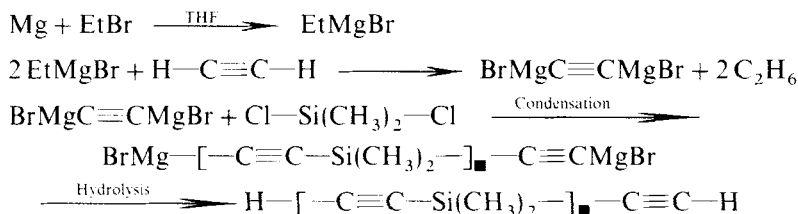
2. EXPERIMENTAL

2.1 Materials

Mg powder, ethyl bromide (EtBr), diethyl ether (Et$_2$O) and 1,3-di-chlorotetramethyldisiloxane (D) were of reagent grade purity and used without further purification. Methyl magnesium bromide (CH$_3$MgBr) was used as 3.0 M in tetrahydrofurane (THF) manufactured by Aldrich. THF was refluxed in the presence of Na wire and purified by rectification under argon gas atmosphere. Dichlorodimethylsilane was used also after rectification under Ar gas atmosphere. CDCl$_3$ used was a special grade reagent, also from Aldrich. The other chemicals were all reagent grade and used as received.

2.2 Synthesis of Ethynyldimethylsilanes (A$_m$s)

All reactions were carried out under Ar atmosphere. A 5,000 mL three-necked round bottom flask was fitted with a Friedrich condenser, dropping funnel, mechanical stirrer and argon inlet. Mg powder (1.33 mole) was placed in the reaction vessel and 3,000 ml of THF were added dropwise with stirring to make a Grignard reagent. After 3 hours the dropping funnel was removed and an ethyne bubbler connected. Ethyne gas was introduced slowly to the reaction vessel after passing through a concentrated H$_2$SO$_4$ layer and a column of activated alumina. As soon as the reaction begun, the solution turned into a white suspension with evolution of heat. The heat effect dropped to undetectable amounts after approximately 4 hours. Then the ethyne bubbler was removed and the dropping funnel reinstalled. Various amounts of dichlorodimethylsilane were dropped carefully into the reaction mixtures. As the reaction proceeded, it became exothermic, the solution color changed to brownish, and a white salt was precipitated. After the reaction was completed, the solvent was removed by evaporation and the residual was hydrolyzed with 1000 ml of 0.1 N HCl. The resulting system was extracted by ether and washed several times with distilled water. The organic layer was separated and dried overnight with MgSO$_4$. After filtering the remaining liquid was evaporated again. Homologs of A$_m$ were separated by vacuum distillation from the residuals and identified as
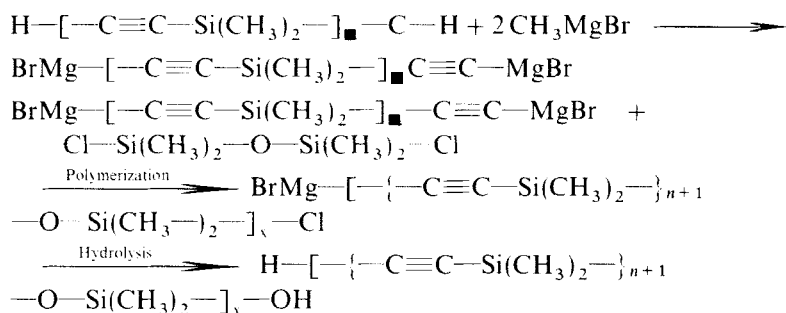
described below. The consecutive stages of the reaction are shown in Scheme 1.

$$Mg + EtBr \xrightarrow{\text{THF}} EtMgBr$$

$$2\,EtMgBr + H—C{\equiv}C—H \longrightarrow BrMgC{\equiv}CMgBr + 2\,C_2H_6$$

$$BrMgC{\equiv}CMgBr + Cl—Si(CH_3)_2—Cl \xrightarrow{\text{Condensation}}$$

$$BrMg—[—C{\equiv}C—Si(CH_3)_2—]_\blacksquare—C{\equiv}CMgBr$$

$$\xrightarrow{\text{Hydrolysis}} H—[—C{\equiv}C—Si(CH_3)_2—]_\blacksquare—C{\equiv}C—H$$

Scheme 1.

2.3 Synthesis of PESSs

Poly(ethynyldimethylsilane-co-dimethylsiloxanes (PESSs) were polymerized as shown in Scheme 2:

$$H—[—C{\equiv}C—Si(CH_3)_2—]_\blacksquare—C—H + 2\,CH_3MgBr \longrightarrow$$

$$BrMg—[—C{\equiv}C—Si(CH_3)_2—]_\blacksquare C{\equiv}C—MgBr$$

$$BrMg—[—C{\equiv}C—Si(CH_3)_2—]_\blacksquare—C{\equiv}C—MgBr \quad +$$

$$Cl—Si(CH_3)_2—O—Si(CH_3)_2—Cl$$

$$\xrightarrow{\text{Polymerization}} BrMg—[—\{—C{\equiv}C—Si(CH_3)_2—\}_{n+1}$$

$$—O—Si(CH_3—)_2—]_x—Cl$$

$$\xrightarrow{\text{Hydrolysis}} H—[—\{—C{\equiv}C—Si(CH_3)_2—\}_{n+1}$$

$$—O—Si(CH_3)_2—]_x—OH$$

Scheme 2.

0.018 mole of an A_m was placed in a 200 mL 3-neck flask. 60 mL of dry THF was transferred into the reaction vessel by an end-to-end syringe under Ar atmosphere. 0.036 mole of methylmagnesium bromide (CH_3MgBr) was introduced into the vessel and the mixture stirred for 4 hours at the room temperature. Then 0.018 mole of 1,3-dichlorotetramethylsiloxane (D) was added. The polymerization lasted 48 hours at 100 C.

The crude product was hydrolyzed with 0.1 N HCl and then extracted by ether, using the same method as before. To remove the salt completely, the product was washed several times with distilled water. The organic layer was separated and evaporated. The resulting

viscous material was diluted with small amounts of ether and precipitated in cold methanol. The number of ethynyldimethylsilane (A) groups in the repeating unit of the resulting polymer was thus changed to $m + 1$. Because the end ethynyl group of A_m reacted with the chlorosilane group of D, ethynylsilane was obtained.

2.4 Instrumental Analysis

A_m and $A_m D$ polymers were characterized by ^{1}H-NMR spectra obtained with a Varian EM 360 spectrophotometer in $CDCl_3$ 99.9% spectral grade (Aldrich Chemicals). FTIR spectra were obtained with a Midac FT-IR apparatus. Gas Chromatography (GC, Hewlett Packard 5890) was used to calculate the composition ratios of A_2, A_3, A_4 and A_5. The initial and final temperatures in the GC analysis were respectively 100°C and 300°C. The initial time was 10 minutes while the heating rate was $10 \text{ K} \cdot \text{min}^{-1}$. The molecular masses and their distributions were determined by gel permeation chromatography (GPC, Maxima 820 GPC Analysis) using polystyrene (PS) standards and THF as the solvent.

Thermal properties of PESSs were determined with a Du Pont thermal analyzer, DSC-2000, and also a Du Pont thermogravimetric analyzer TGA-2100. Calibration of the DSC apparatus was performed with indium as the standard (the melting temperature T_m of indium $= 156.8°C$, its enthalpy of fusion $H_{fus} = 28 \text{ J} \cdot \text{g}^{-1}$ [19]). The heating rates were $10 \text{ K} \cdot \text{min}^{-1}$ in DSC and $30 \text{ K} \cdot \text{min}^{-1}$ in TGA.

The morphology of the crystalline phases was observed with a polarizing microscope of Leitz, Wetzlar, Germany, the Ortoplan model.

3. RESULTS AND DISCUSSION

3.1 Identification of A_ms

FTIR spectrum of A_2 is shown in Figure 1. The absorption bands around 2040 cm^{-1} and 3300 cm^{-1} are known [20] to represent respectively the $C \equiv C$ and $C \equiv C$—H stretching modes. The bands at 1260 cm^{-1} and $750-800 \text{ cm}^{-1}$ are assigned to Si—CH_3 groups. If the chlorosilane Si—Cl group remained as the end group of the product,
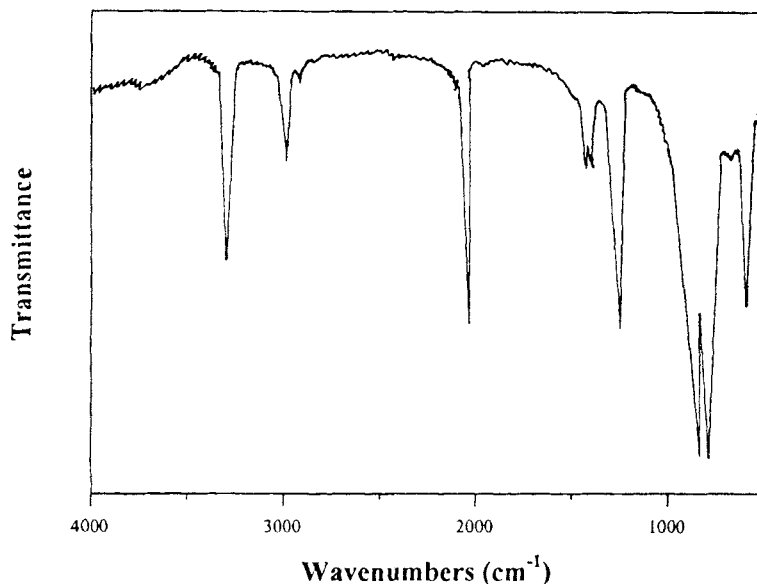
FIGURE 1   FT-IR spectrum of A_2.

it should turn into hydrosilane Si—OH by hydrolysis. However, in Figure 1 we cannot find a band at $3700 \, cm^{-1}$ which corresponds to the Si—OH stretching. Thus, our product does not contain chlorosilane groups.

As the next step, we have analyzed the ^{1}H-NMR spectrum of A_2; see Figure 2. Peaks are located at $\delta = 2.4$ and also $0.00 \leqslant \delta \leqslant 0.04$. They have been assigned respectively to the protons of C≡C—H and Si—CH$_3$; the integral ratio of these peaks is 1:6. We find that the FTIR and the NMR spectra lend themselves to the same conclusions, and thus we have verified the synthesis of A_m with $2 \leqslant m \leqslant 5$. Basic physical properties of A_ms so synthesized are listed in Table I.

Inspection of Table I shows that the melting temperature T_m of A_3 is lower than that of A_2. This is a manifestation of the odd-even effect, observed by a number of authors and explained for instance in [12] or [13]. We see in the same Table that the boiling temperatures T_b of A_2 and A_3 are quite different — what makes possible virtually complete separation of these two components by vacuum distillation. By contrast, A_4 and A_5 have boiling temperatures at the pressure $P = 0.5$
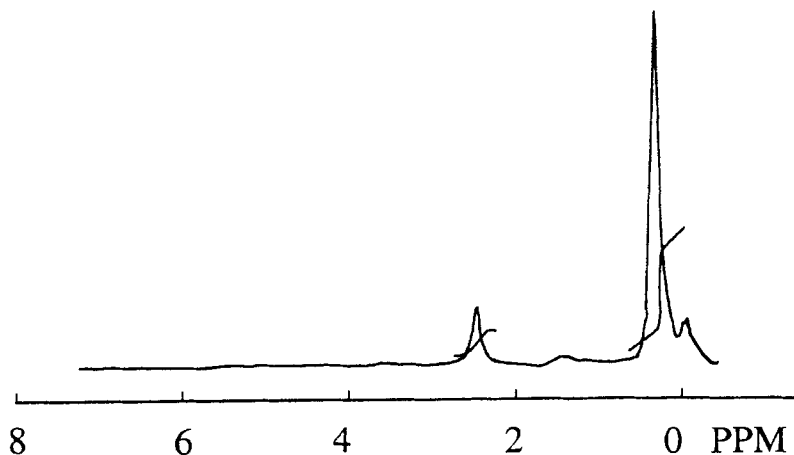
FIGURE 2 ^{1}H-NMR spectrum of A_2 in CDCl.

Torr close to each other, hence separation along this route cannot be accomplished.

To determine the compositions accurately, the response factor (RF) was calculated from the GC analysis [21]. Dodecane was used as the standard. The yields of A_ms were computed from RF values and integrations of GC diagrams; the results are summarized in Table II. We infer from this table that the molar ratios of the reactants constitute an important factor affecting the chain length m of A_ms. Since both reactants, di-Grignard and ethyne and dichlorodimethylsilane, have difunctional groups, the reactions occur by condensation. Using smaller amounts of the silane was desirable since we aimed at products which have the ethynyl group at both ends. However, if *too* small amounts of the silane were used, the resulting m value of A_m was too low; Table II shows that by using larger amount of the silane one

TABLE I   Physical Properties of A_m

m	$T_m/°C$	$T_b/°C$ at 0.5 mm Hg
2	58 – 59	85 – 86
3	38 – 39	124 – 126
4	67 – 68	137 – 139

TABLE II   The Yields of Products and the Reaction Ratios

| Molar reaction ratios		Yields* in %				
BrMgC≡CMgBr	Cl-Si(CH₃)2-Cl	A2	A3	A4	A5	Total
1	0.6	18.2	15.2	5.1	1.1	39.6
1	0.7	20.3	16.3	5.7	3.6	45.9
1	0.8	24.9	18.2	7.5	3.6	54.2
1	0.85	14.6	25.3	10.0	5.7	55.6
1	0.9	7.2	11.3	6.6	6.1	31.2

*These yields were calculated on the basis of dichorodimethylsilane used.

achieves larger m values. The yields are relatively low; this can be explained by two factors. First, a part of A_1 is removed during solvent evaporation because it has a low boiling point (indeed, its presence was detected in the vacuum trap). On the other hand, products higher than A_6 cannot be separated by vacuum distillation; they remain as residues because of their high boiling points. When the molar reactivity ratio of the di-Grignard ethyne and dichlorodimethylsilane used was 1:09, the yields decreased rapidly; this constitutes the second pertinent factor.

3.2   Identification of Poly(A$_m$D)s

Figure 3 shows the FTIR spectrum of poly(A_5D). The broad band around $1100\,cm^{-1}$, known to correspond to Si—O—Si [20], is clearly visible for this polymer. However, there is no such band in the A_4D spectrum. ^{1}H-NMR spectrum of poly(A_5D) has been obtained as well (Fig. 4). As before, the peaks at $\delta = 2.4$ and also $0.00 \leqslant \delta \leqslant 0.04$ have been assigned respectively to the protons of C≡C—H and Si—CH$_3$. The integral ratio of these peaks is 1:160. Apparently nearly all the protons attached to the ethynyl group in A_5 have reacted and the polymerization has taken place.

A_mD polymers with $m \neq 5$ have been investigated in the same way; for brevity we do not include the respective spectra. For all the polymers we have determined molecular masses (molecular weights, MWs) and molecular mass distributions (molecular weight distributions, MWDs) by GPC. The resulting polymerization yields, MWs and MWDs are summarized in Table III. We see that the yields are relatively high. The polymers obtained have MWs in the range

Wavenumbers (cm⁻¹)
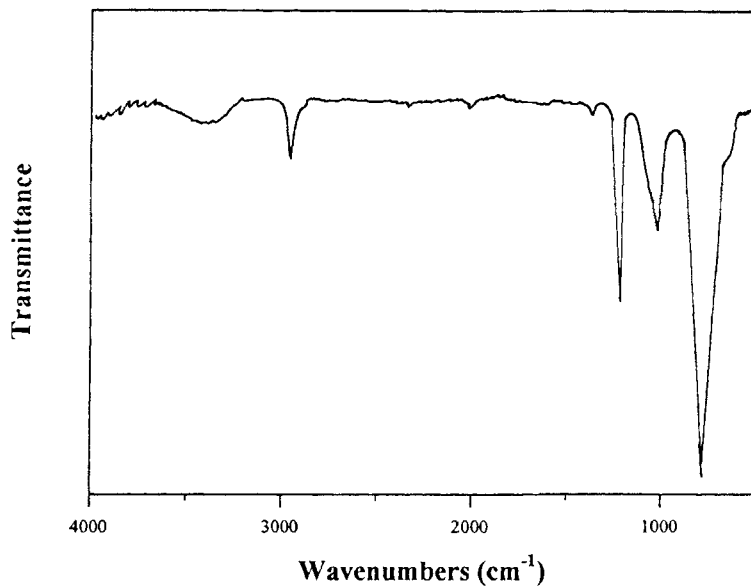
FIGURE 3   FT-IR spectrum of the A₅D polymer.
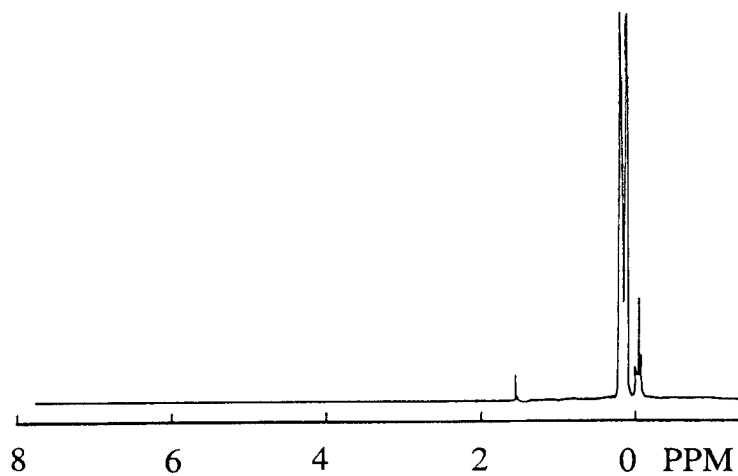
FIGURE 4   ¹H-NMR spectrum of the A₅D polymer.

between 10 and 20 thousands. In Section 1 we have noted the results of Iwara *et al.* [8] and also of Luneva and coworkers [10, 11] whose MW values were quite low. Our molecular weights are already in the range which can be of interest to industry.

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TABLE III The Polymerization Yields. M_w and $M_w D$ of Poly($A_m D$)

Polymer	m	Yield(^o_o)	$M_w{}^a$	$M_w{}^b$	M_w / M_n
P-V	5	51	14.000	10.000	1.4
P-IV	4	76	19.000	10.000	1.9
P-III	3	66	14.000	7.000	2.0

$^a M_w$ is the weight-average molecular weight.
$^b M_n$ is the number-average molecular weight.

3.3 Thermal Properties of Poly(A_mD)s

Four DSC runs were made for each of the polymers obtained. In each case virtually the same results were obtained in all runs. A DSC thermogram for $A_5 D$ (labelled also P-V in Tab. III) is shown in Figure 5; a corresponds to the first and b to the second run. In the first run the material shows the glass transition temperature $T_g = -12.6°C$, the melting temperature $T_m \approx 40°C$ and a cold crystallization region with the maximum around $16°C$. In the second run the melting peak
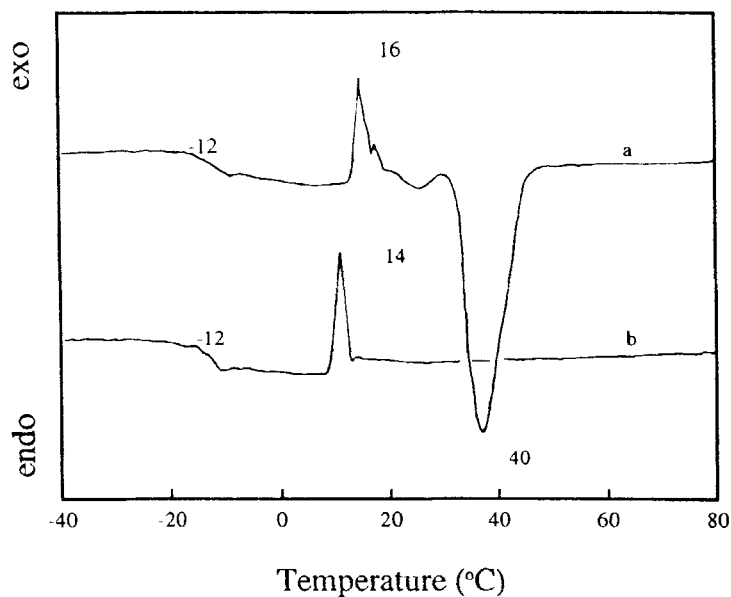

FIGURE 5 DSC thermograms of $A_5 D$ polymer. (a) first run; (b) second run.

does not appear, while the glass transition and the cold crystallization do; this happened also in all four DSC experiments. This peculiar phenomenon may be related to the stability of the crystalline phase. However, West *et al.* [22] and Allen *et al.* [23] explained such a behavior by the formation of a liquid-crystalline (LC) mesophase. Our A_5D is quite stable; no further transitions were observed up to tempratures exceeding 200°C. It is known that the clearing (isotropization) temperatures of polymer liquid crystals (PLCs) are relatively high [12–14]. PLCs are mostly copolymers consisting of flexible and LC sequences; the latter are relatively rigid. Thermal stability at elevated temperatures exhibited by A_5D is typical for PLCs - in contrast to engineering polymers which are generally flexible and usable at lower temperatures.

To acquire further information, phase structures of A_5D were observed under a polarizing microscope with a temperature controller; selected micrographs are shown in Figure 6. We see in Figure 6a that A_5D has melted at 40°C. However, Figure 6b shows a different phase at 60°C. Moreover, the latter did not change even when heated
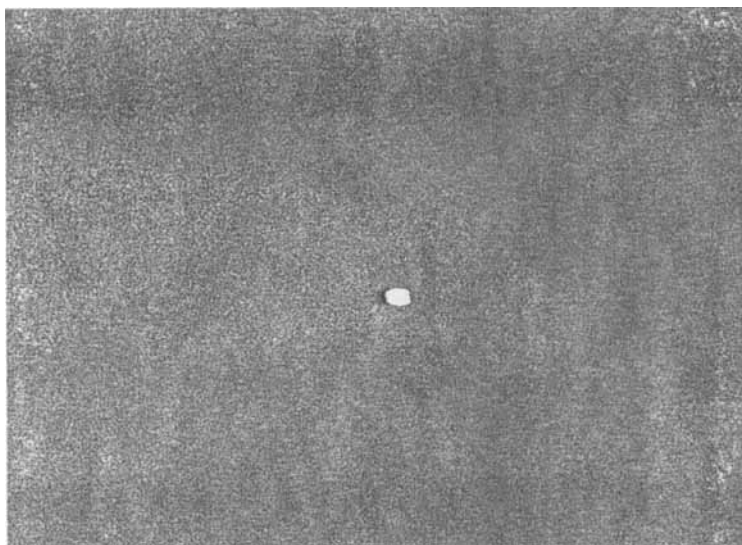

FIGURE 6a   Polarized optical micrographs of the A_5D polymer. Magnification X 272. (a), 40°C; (b), 60°C; (c), 150°C.
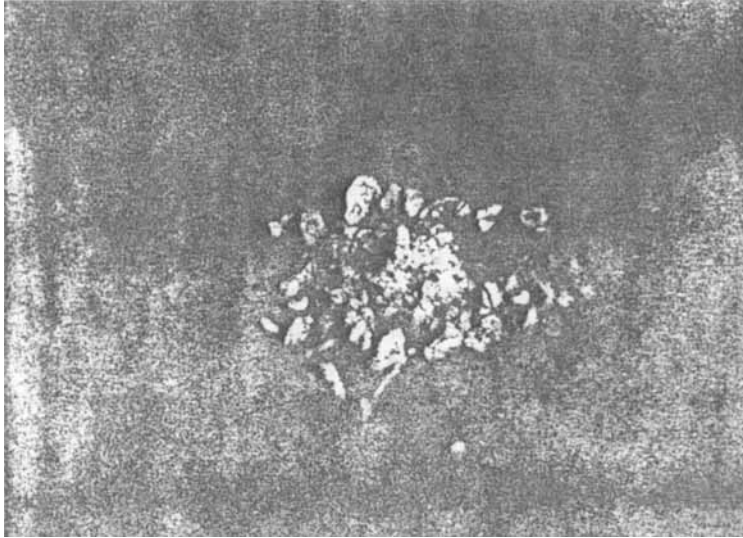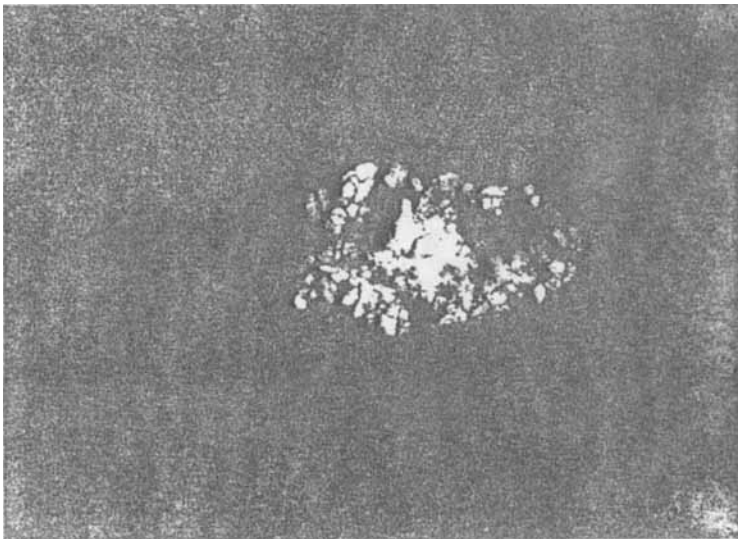
FIGURE 6b   (Continued).

FIGURE 6c   (Continued).

to 150°C – as visible in Figure 6c. Thus, also from the polarizing microscopy results we infer that $A_5 D$ forms a liquid-crystalline phase.

On the other hand, the phenomena described above did *not* occur in $A_3 D$ and $A_4 D$. We display in Table IV thermal properties of $A_3 D$, $A_4 D$ and $A_5 D$. As can be seen in the Table, the glass transition and melting temperatures of the $A_m D$ series homologs go symbatically with the chain length m of A. This result might be due to the relatively high stiffness of the ethynyl group; polymers with more ethynyl groups exhibit higher melting and transition temperatures. In the case of $A_3 D$ melting and cold crystallization were not observed; clearly this polymer is amorphous.

Thermal stabilities of the $A_m D$ polymers were determined by using TGA. The results for $A_5 D$ are shown in Figure 7. We see that thermal

TABLE IV Thermal properties of poly($A_m D$)

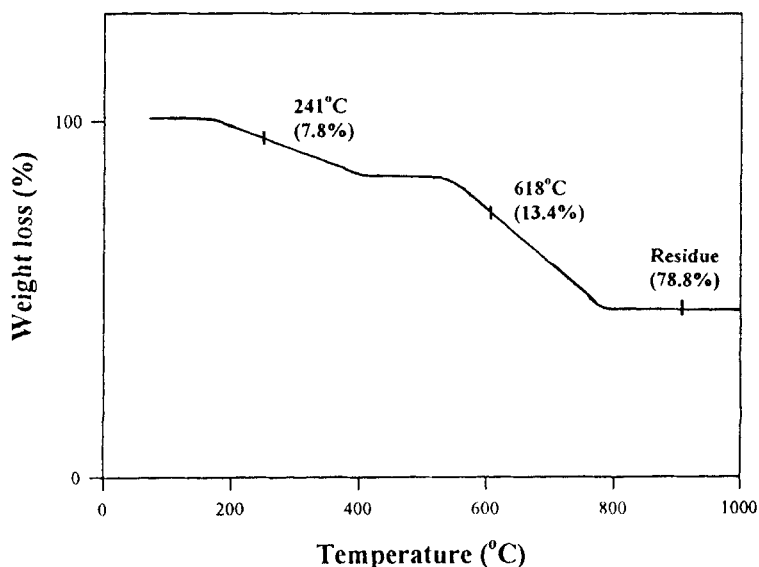| Polymer	m	$T_g/°C$	$T_c/°C$	$T_m/°C$
P-V	5	−12.6	15.8	40
P-IV	4	−16.1	−8.3	12
P-III	3	−23.0	−	−

FIGURE 7 TGA thermograms of the $A_5 D$ polymer.

degradation takes place in two regions, once around 250°C and then again around 600°C. These can be attributed respectively to the degradation of ethnylsilane and siloxane [24]. We note that A_5D retains 78.5 wt. % of the residue even when heated up to 1000°C.

4. SOME CONCLUDING REMARKS

Through the combination of ethynyl group as the rigid one and siloxane as the flexible one, we have tried to find an optimum combination showing the characteristics of a polymer liquid crystal. We have obtained at least one polymer which exhibits LC properties. It turns out that A_2 has a higher melting point than A_3, what represents one more manifestation of the odd-even effect [12, 13]. To obtain a product with ethynyl groups at both ends, we have employed with success d-Grignard ethyne and dichlorodimethylsilane in the 1:0.8 ratio. Poly(ethynyldimethylsilane-co-dimethylsiloxanes) synthesized by a condensation reaction of A_m and 1,3-dichlorotetramethyl-disiloxane have been obtained with relatively high yields and with molecular weights sufficient so as to be of interest to industry. When the m value in A_5Ds was lower than 3, the crystallinity was absent. In the case of poly(A_5D) a LC mesophase is obtained. All polymers which have been obtained in this study exhibit very good thermal stabilities.

Acknowledgement

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