Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Gal, Yeong-Soon , Lee, Won-Chul , Lee, Hyong-Jong , Jang, Sang-Hee and Choi, Sam-Kwon(1997) 'Cyclopolymerization of Diethyl Dipropargylmalonate and Triethyl Dipropargylphosphonoacetate by Molybdenum Pentachloride', Journal of Macromolecular Science, Part A, 34: 11, 2251 — 2267

To link to this Article: DOI: 10.1080/10601329708010045

URL: http://dx.doi.org/10.1080/10601329708010045

J.M.S.—PURE APPL. CHEM., A34(11), pp. 2251–2267 (1997)

CYCLOPOLYMERIZATION OF DIETHYL DIPROPARGYLMALONATE AND TRIETHYL DIPROPARGYLPHOSPHONOACETATE BY MOLYBDENUM PENTACHLORIDE

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ABSTRACT

The cyclopolymerizationof two dipropargyl monomers having different functionality (diethyl dipropargylmalonate, triethyl dipropargylphosphoneacetate) was carried out by molybdenum (V) chloride catalyst system in chlorobenzene at 60°C. The polymerizations were well proceeded to give a high polymer yield (85-98%). The number average molecular weights (Mn of poymers were in the range of 46000—97000. These polymers were completely soluble in aromatic and halogenated hydrocarbon solvents and easily casted into a homogeneous polymer film. Various instrumental analyses such as NMR (^{1}H- and ^{13}C-), IR, GPC, and UV-visible spectroscopies indicated that the present polymers have a highly conjugated polymer backbone structure. The tensile strength and failure strain of polymer film generally increased as the feed ratio of diethyl dipropargylmalonate in copolymer increased. On the other hand, the char yield of polymers increased significanly as the feed ratio of triethyl dipro-pargylphosphonoacetate in copolymer increased.

INTRODUCTION

The polymerization of acetylene and its derivatives in the presence of organometallic catalysts, anionic, cationic, and other initiators has been studied in some details for the fast four decades [1-5}. This method is one of the fundamental methods for the synthesis of polymers having a conjugated system. The simplest of conjugated polymers, polyacetylene, has been synthesized with a wide variety of catalysts [6, 7], of which the procedure described by Shirakawa *et al*. [8-10] has received the most attention. However, polyacetylene is unstable toair oxidation in air and insoluble in the usual organic solvents. In order to increase the solubility of conjugated polymers and provide the various functionalities of the polymer, various substituted polyacetylenes have been synthesized and characterized [11-15], although the electrical conductivity is somewhat low.

These polymers have been used as organic semiconductors [16, 17), liquidmixture separation [18-20], side-chain liquid crystals [21-23), and electron-beam resist (radiation degradation) [24-26].

In recent years, organic compounds with π–electron delocalization are of wide interest as nonlinear optical materials with potential applications as optical switches and other nonlinear optical devices [27-29]. Polymers are considered to be leading candidates for future optical photonic devices because they can be modified by molecular engineering and can be produced in various forms,including waveguides, films, fibers, and single crystals. Solution or thin films of conjugated polymers have been reported to have third-order electric susceptibilities $\chi^{(3)}$ ranging from 10^{-12} to 10^{-9} esu.

The cyclopolymerization of diethyl dipropargylmalonate (DEDPM) yielded a completely soluble conjugated polymer having high molecular weights (max. Mn: 127,000) [30]. The studies on the nonlinear optical properties and the applications as optical image process of poly(DEDPM) were widely carried out [31, 32].

The interesting features of phosphorous polymers are flame-retarding characteristics, adhesion to metals, metal ion-binding characteristics, and increased polarity [33]. Phosphorous containing polyacetylenes are expected to show properties and functions peculiar to their structure. At present, it is very interesting to combine of DEDPM polymer and phosphorous-containing acetylene polymer.

Now we report the synthesis of novel conjugated cyclopolymer by the cyclcopolymerization of DEDPM and triethyl dipropargylphosphonoacetate (TDPA) by transition metal catalyst and the properties of resulting conjugated cyclopolymers having different functionalities.

EXPERIMENTAL

Materials

Diethyl malonate (Aldrich Chemicals, 99%) was dried over calcium hydride and distilled at reduced pressure. Propargyl bromide (Aldrich Chemicals, 80 wt% solution of toluene) was dried over calcium hydride and fractionally distilled. Triethylphosphonoacetate (Aldrich Chemicals, 99%) was used as received.

Molybdenum (V) chloride (Aldrich Chemicals., resublimed, 99.9+%) were used without further purification. All solvents were used after purification according to the conventional methods.

Instruments

NMR (^{1}H- and ^{13}C-) spectra were recorded on Bruker AM-200 spectrometer in $CDCl_3$. Infrared spectra were obtained with a BOMEN Michelson using potassium bromide pellets. UV-visible spectra were obtained with a Cary 17 spectrometer with Aminco-Y recorder. The average molecular weights of polymers were measured by means of GPC-150C of Waters using a calibration curve for polystyrene. Elemental analyses were performed with Carlo Erba EA 1108 Elemental Analyzer. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min up to 650°C with a DuPont 1090 Analyzer.

Synthesis of Diethyl Dipropargylmalonate (DEDPM) [30]

Diethyl malonate (40g, 0.25 mol) was added to the absolute ethanol (200mL) containing sodium ethoxide (from sodium, 12.6g, 0.55mol). After 5 minutes, propargyl bromide (65.5g, 0.55 mol) was slowly added to the stirred suspension. In this case, the temperature did not exceed 60°C. Then the mixture was heated under reflux condition for 12 hours. After removal of the alcohol under reduced pressure, the residue was diluted with water, and the neutral fraction was isolated and dissolved in hexane. Diethyl dipropargylmalonate (46.6g, 0.2 mol) was slowly separated in needle form. Yield; 79%, mp 46°C. Elemental analysis: Calcd for $C_{13}H_{16}O_4$: C, 66.08%; H, 6.84%; O, 27.08%. Found: C, 66.10%; H, 6.79%; O, 27.11%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.230 (t, J = 2.54, 6H), 2.0 (t, J = 2.54, 2H), 2.96 (d, J = 2.56, 4H), 4.21 (q, J = 7.17, 4H). ^{13}C-NMR ($CDCl_3$ δ, ppm): 14.8 ($-CH_3$), 23.5 ($CH_2C\equiv$), 56.3 (-C-), 63.0 $-OCH_2-$), 72.9 ($\equiv$C-H), 79.6 (-C$\equiv$), 169.4 (C=O), IR (KBr pellet, cm- ^{1}): 3310 ($\equiv$C-H), 1715 (C =O).

Synthesis of Triethyl Dipropargylphosphonoacetate (TDPA) [34]

Triethylphosphonoacetate (22.4g, 0.1 mol) was added dropwise to dry THF (200mL) containing sodium hydride (5.5g, 0.23mol) for 1 hour. Then, propargyl bromide (32g, 0.2 mol) was slowly added to the reaction mixture and stirred under ambient temperature for 12 hours. After the water was added to quench the reaction, the solution was extracted with ether, then, the extracted layer was dried over anhydrous $MgSO_4$. TDPA was purified by vacuum distillation after evaporating the ether. Yield: 72%, bp 132°C/0.5mmHg. Elemental analysis: Calcd for $C_{14}H_{21}PO_5$: C, 55.99%; H, 7.06%; P, 10.31%; O, 26.64%. Found: C, 55.85%; H, 7.05%; P, 10.21%; O, 26.89%. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.31 (q, J = 7.09, 9H), 2.04 (t, J = 2.74, 2H), 2.97 (d of d, J = 2.75, 2H of $CH_2C\equiv$, 3.04 (d of d, J = 1.4, 2H), 4.21 (m, 6H). ^{13}C-NMR ($CDCl_3$, δ ppm): 13 ($-CH_3$ of ester),16 ($-CH_3$ of phosphonate), 21 ($-CH_2-$ of $CH_2C\equiv$), 49.5 (C of P-C-), 61.9 ($-OCH_2$ of ester), 63 ($-OCH_3$ of phosphonate), 71 ($\equiv$CH), 79 (-C$\equiv$), 168.7 (C=O), ^{31}P-NMR ($CDCl_3$, δ ppm): 22.28, IR (neat, cm^{-1}): 3200 ($\equiv$C-H), 1732 (C=O), 1239 (P=O).

Polymerization Procedures

All procedures for catalyst solution preparation and polymerization were carried out under nitrogen atmosphere. Molybdenum (V) chloride ($MoCl_5$) was dissolved in chlorobenzene as 0.1 M solution before use. A polymerization ampule equipped rubber septum was flushed with dry nitrogen. Injections of solvent, catalyst solution, and comonomer were done by means of hypodermic syringes from which air and moisture were carefully excluded.

Copolymerization of DEDPM and TDPA by $MoCl_5$

A solution of $MoCl_5$ (0.67 ml 0.1 M chlorobenzene solution, $0.67x10^{-5}$mol) and chlorobemzene (5mL) is prepared. To this solution is added the comonomer mixture (0.89g, DEDPM/DPPA, (0.5g/0.39g), comonomer feed ratio:1/1) at room temperature. Then, the polymerization was carried out at 60°C for 24 hours. After the polymerzation time, 10mL of chloroform was added to the ampoule. This polymer solution was precipitated into excess hexanes, filtered from the solution, and then dried under vacuum at 40°C for 6 hours. The polymer yield was calculated by gravimetry. By changing the comonomer feed ratios, the copolymers with other composition were similarly prepared.

Preparation of Polymer Film

THF solutions of the polymers were casted on a Petri dish, and then the solvent was evaporated slowly at ambient temperature over several days. The polymer films obtained were kept in a vacuum oven (ca. 0.1 mmHg) for 48 hours in order to remove the occluded solvents as completely as possible. The films were homogeneous and had uniform thickness. The film thickness was measured by a micrometer.

Measurement of Electrical Conductivity

The electrical conductivity of iodine-doped polymer film was determined using a standard four-point probe technique. The distance of each probe, which was made from platinum, was 1 mm. The conductivity is given by the formula that follows:

$$\sigma = \frac{1}{2\pi S} \times \frac{I}{V}$$

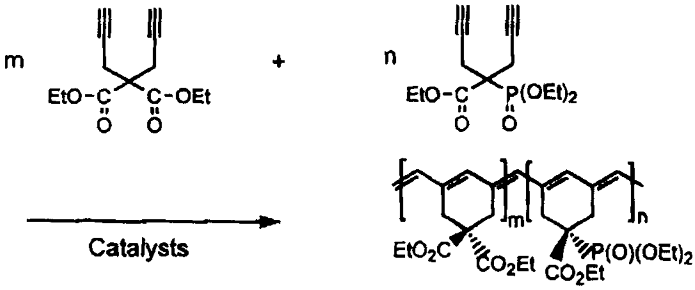
Where σ is the electrical conductivity ($\Omega^{-1}cm^{-1}$); S, the distance between each probe; and I and V, the current and the voltage, respectively.

Test of Mechanical Properties

Tensile tests of polymer films were carried out at 20°C at a crosshead speed of 1 mm/min by using Instron Tensile Tester (No 1122). The specimen size was 33 x 10 x 0.05 mm. The calculation methods of mechanical properties from experiments are as follows:

- Tensile strength, $\sigma = \frac{W}{A_o}$

-Young's modulus, $E = \frac{\Delta\sigma}{\Delta\varepsilon}$



SCHEME 1. Cyclopolymerization of DEDPM and TDPA.

-Ultimate strain, $\varepsilon = \frac{L-L_o}{L_o} \times 100\ (\%)$

Where, W: maximum bad

A_0: initial cross-sectional area

$\Delta\sigma$: increment of stress

$\Delta\varepsilon$: increment of strain

L: gage length at failure

L_0: original gage length

RESULTS AND DISCUSSION

Polymerization

The cyclopolymerization of two dipropargyl monomers, DEDPM and TDPA, having different monomer feed ratios was carried out by molybdenum (V) chloride (Scheme 1).

The homopolymerization of DEDPM alone by $MoCl_5$-based catalysts proceeded well to give a high yield of polymer having high molecular weight $\overline{Mn}$: 61000-127000 [30]. It was found that the $MoCl_5$-based catalysts are very effective for the cyclopolymerization of another monomer containing phosphorous atom, TDPA (polymer yield $\geq$ 76%, $\overline{Mn}$: 22000-46000) [34]. In the present cyclocopolymerization of DEDPM and TDPA, the catalytic activities of $MoCl_5$-based catalysts were found to be more effective than those of WCl_6-based catalysts. The polymer yields, when the $MoCl_5$ is used alone, were found to be signicantly higher

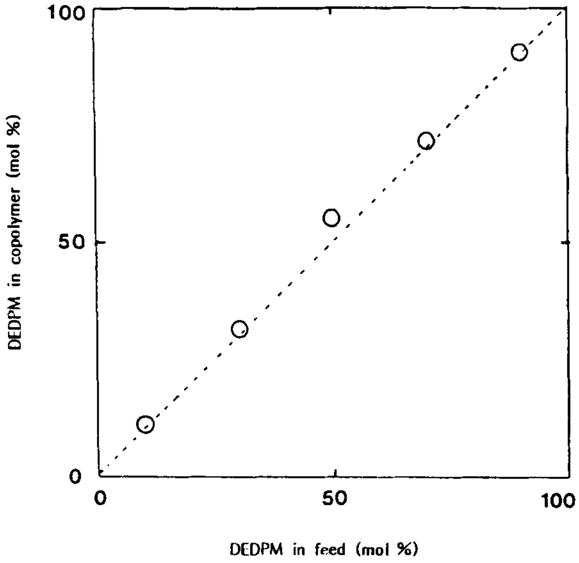


Figure 1. Composition curves for the copolymerization of DEDPM and TDPA by $MoCl_5$.

than those in the cases of using the cocatalysts ($EtAlCl_2$, n-Bu_4Sn). Thus, we used the $MoCl_5$ as the catalyst for the cyclopolymerization of DEDPM and TDPA. The present polymerization was deduced to proceed via the cyclization process because there are no insoluble products, which is originated from the non-ideal cyclopolymerization process.

Figure 1 shows the composition curves for the cyclopolymerization of DEDPM with TDPA. The shapes of composition curves suggest that random copolym-erization was taking place. This also means that the reactivities of two monomers are similar.

Table 1 shows the typical results for the cyclocopolymerization of DEDPM and TDPA by $MoCl_5$. The monomer to catalyst mole ratio (M/C) was 50. The yields of homopolymerization for DEDPM and TDPA by $MoCl_5$ were 91% and 98%, respectively. The polymer yields for the copolymerization of DEDPM and TDPA according to the comonomer feed ratios were in the range of 85% and 89%. The number average molecular weights $\overline{Mn}$: and the polydispersities ($\overline{Mw}$ / $\overline{Mn}$) of three copolymers were 49000-61000 and 2.5-3.5, respectively. The polymer yields were slightly lower at the copolymerization in comparison with the homopolymerization, although the reason is not clear.

TABLE 1. Cyclocopolymerization of DEDPM and TDPA by $MoCl_5$[a]

Exp. No.	Feed ratio of DEDPM/TDPA	Polymer yield[b] (%)	GPC[c] $\overline{M}n/10^3$	$\overline{M}w/\overline{M}n$
1	100/0	91	97	2.8
2	75/25	89	56	2.7
3	50/50	85	61	3.5
4	25/75	86	49	2.5
5	0/100	98	46	3.2

[a] Polymerization was carried out at 60 °C for 24 hours in chlorobenzene. Monomer to catalyst mole ratio (M/C) and initial monomer concentration ([M]o) were 50 and 0.25, respectively.

[b] The precipitated copolymers in hexane were gravimetrically estimated.

[c] Values were obtained by GPC analysis with polystyrene standards.

Polymer Structure

The polymers structure was characterized by various instrumental methods such as NMR (^1H-, ^{13}C-), IR, and UV-visible spectroscopies. Figure 2 shows the ^1H-NMR spectra of homopolymer (poly(DEDPM) and poly(TDPA)] and copolymer (feed ratio of DEDPM/TDPA = 1/1) in $CDCl_3$. The acetylenic proton peaks at 2.1 ppm for DEDPM and 1.96 ppm for TDP\A did not appear in the ^1H-NMR spectra of polymers. Instead, a broad peak due to the protons on the conjugated double bonds of polymer main chain was observed in the range of 6.0-7.2 ppm. In the ^1H-NMR spectrum of poly(TDPA), the methylene protons (2.9 ppm, doublet of doublet), which couple with both adjacent phosphorous and acetylene protons, shift to the broad peak around 3.4 ppm. In the ^1H-NMR spectrum of copolymer (feed ratio of DEDPM/TDPA = 1/1), the characteristic peaks of two homopolymers were simultaneously observed). The broad peak at 2.55 ppm, which is a characteristic one of poly(TDPA), was originated from the moisture absorbed by the highly higroscopic properties of poly(TDPA) moiety. The same peak was also observed at 2.3 ppm at the ^1H-NMR spectrum of copolymer. However, the moisture peak was not observed in the ^1H-NMR spectrum of poly(DEDPM).

Figure 3 shows the ^{13}C-NMR spectra of polymers in $CDCl_3$. The ^{13}C-NMR spectra of polymers did not show the acetylenic carbon peaks at 72.9,

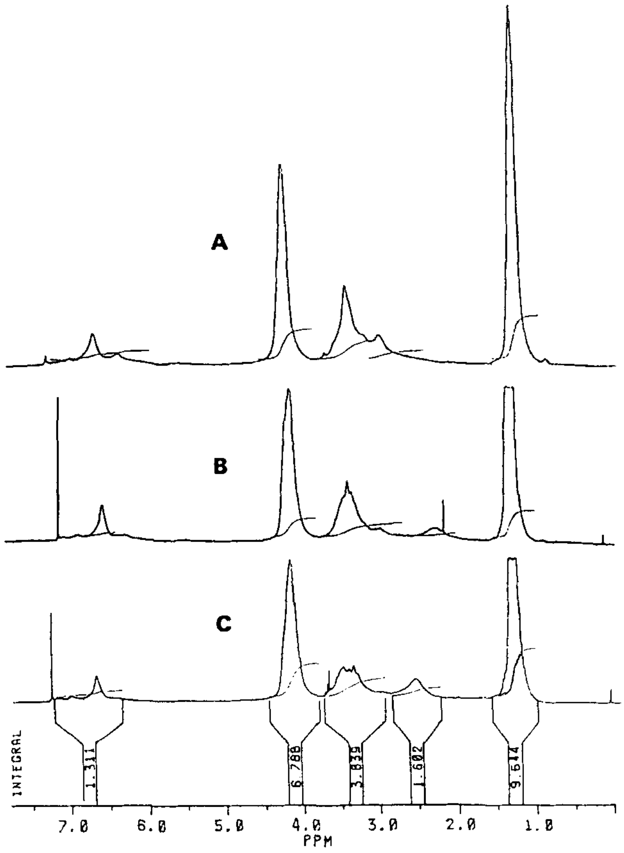


Figure 2. ^{1}H-NMR spectra of poly(DEDPM) (A), copolymer (feed ratio of DEDPM/TDPA = 1/1, (B), and poly(TDPA) (C)) in $CDCl_3$.

79.7 ppm for DEDPM and 71.3, 79.5 ppm for TDPA. Instead, the carbon peaks of the polyene backbone were appeared at 123 and 136 ppm for poly(DEDPM) and 123.3 and 137.3 ppm for poly(TDPA). In the ^{13}C-NMR spectrum (B) of copolymer (monomer feedratio = 1:1), the characteristic carbon peaks were observed at the region of olefinic and carbonyl carbons. However, two methyl carbon peaks were observed at 13.95 ppm and 16.43 ppm, which originated from poly(DEDPM) and poly(TDPA), respectively. Also, the peak intensity of methylene carbons adjacent to the ester group increased as the feed ratio of DEDPM in copolymers increased.

Figure 4 shows the IR spectra of polymers in KBr pellet. These spectra showed no absorptions at the acetylenic ≡C-H stretching frequencies (3310 cm^{-1} for

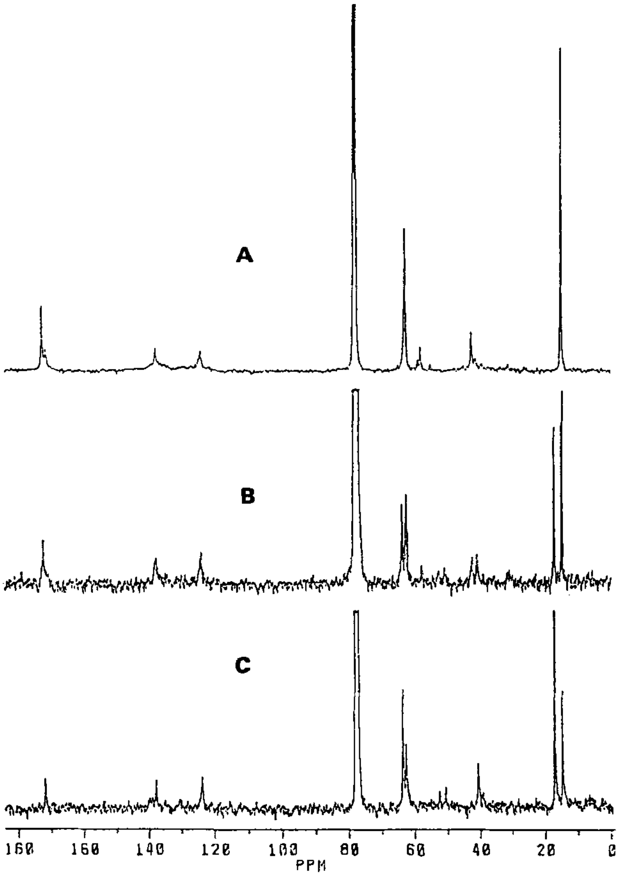


Figure 3. ^{13}C-NMR spectra of poly(DEDPM) (A), copolymer (feed ratio of DEDPM/TDPA = 1/1, (B), and poly(TDPA) (C)) in $CDCl_3$.

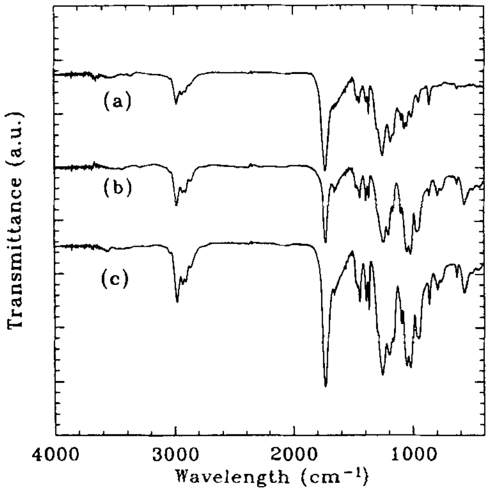


Figure 4. FT-IR spectra of two homopolymers [poly(DEDPM) (A), poly(TDPA) (B)] and copolymer (feed ratio of DEDPM/TDPA = 1/1, (C) in KBr pellet.

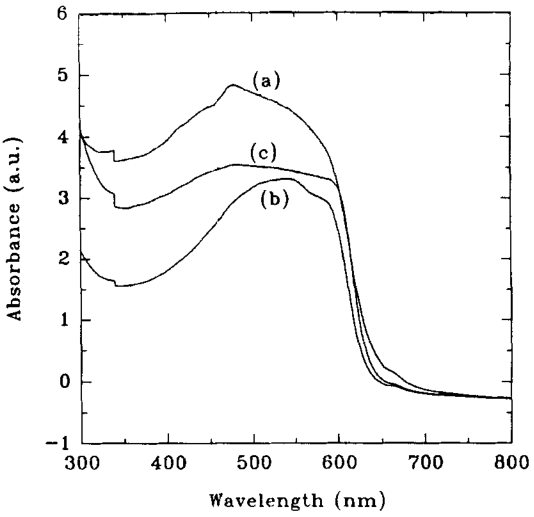


Figure 5. UV-visible spectra of two homopolymers [poly(DEDPM) (A), poly(TDPA)(B)] and copolymer (feed ratio of DEDPM/TDPA = 1/1, (C) in tetrahydrofuran.

DEDPM, 3210 cm^{-1} for TDPA) and the acetylenic C ≡ C stretching frequencies which were presented for the dipropargyl monomers. Instead, weak and broad absorption peaks at 1610-1670 cm^{-1}, resulting from the conjugated double bonds of the polymer backbone, were recently observed. The strong peaks at 1787 cm^{-1} is due to the C=0 stretching frequencies of ester.

The UV-visible spectra of the polymers were measured in THF solvent (Figure 5). These polymers showed characteristic broad peaks (bathchromic shifts) in the regions of 400-650 nm., that is due to the $\pi \rightarrow \pi^*$ transition of conjugated polymer backbone.

Polymer Properties

The mechanical properties of polymer films were also tested and evaluated. The test results of tensile properties of polymer films are shown in Table 2. The tensile strength decreased from 90 MPa for poly(DEDPM) homopolymer to 37 MPa for poly(TDPA) homopolymer as the feed ratio of TDPA in copolymer increased. The tensile modulus also decreased signifcantly from 4300 MPa for poly(DEDPM) homopolymer to 1650 MPa for poly(TDPA) homopolymer as the feed ratio of TDPA in the copolymer increased. The ultimate failure strain was in the range from 1.6% to 3.2%.

TABLE 2. Tensile Properties of the Polymer Films from DEDPM and TDPA.

Exp. No	Comonomer feed ratio (DEDPM/TDPA)	Tensile strength (σ_B MPa)	Young's modulus (E, MPa)	Ultimate strain(%)
1	100/0	90	4300	3.2
2	75/25	78	3450	2.6
3	50/50	65	2040	2.2
4	25/75	51	1950	1.7
5	0/100	37	1650	1.6

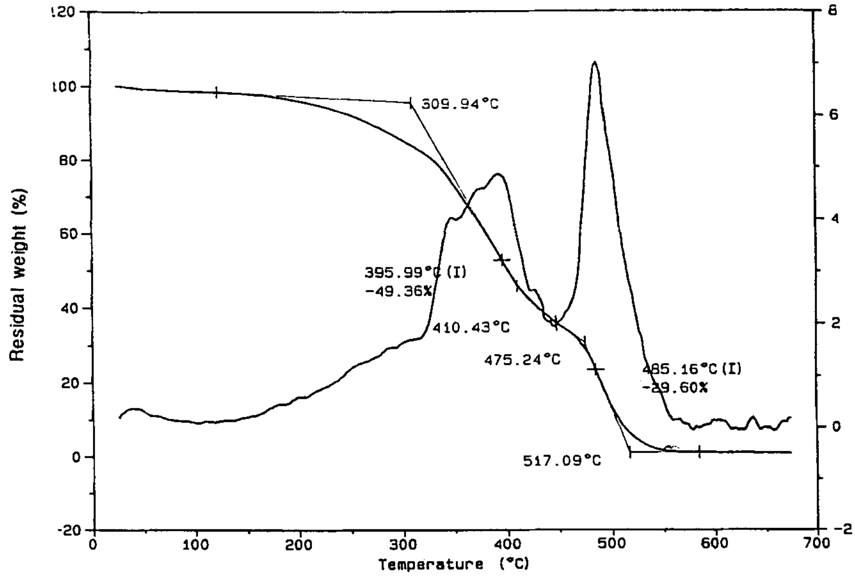


Figure 6. TGA thermogram of poly(DEDPM).

It was thought that the enhanced mechanical properties of poly(DEDPM) homopolymer originated from its high molecular weight and the excellent film castability of the poly(DEDPM). On the other hand, the test of mechanical properties on poly(DEDPM) film having a low molecular weight ($\overline{M}n \leq 1000$) was impossible since the polymer film was very brittle.

In order to elucidate the thermal properties according to comonomer feed ratio, the thermogravimetric analyses of these polymers were carried out under

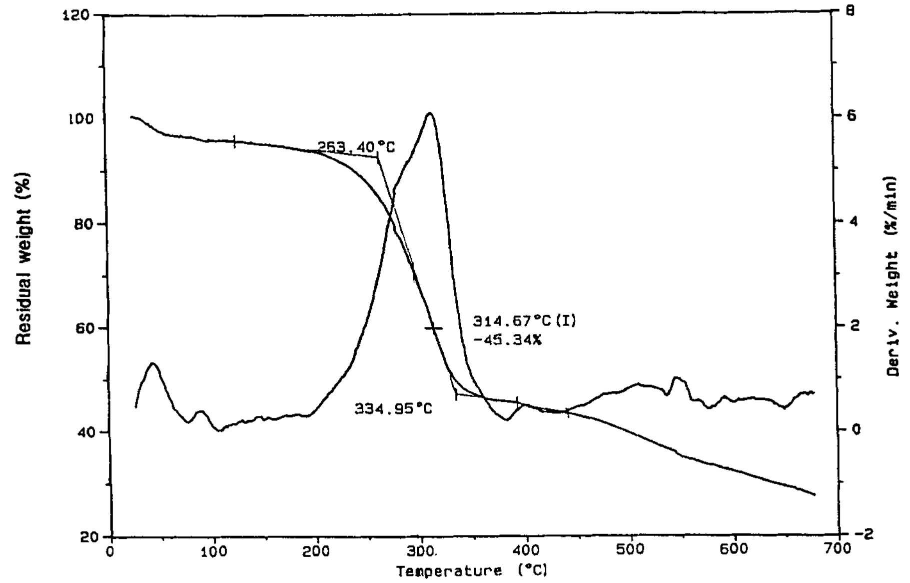


Figure 7. TGA thermogram of copolymer (feed ratio of DEDPM/TDPA = 1/1).

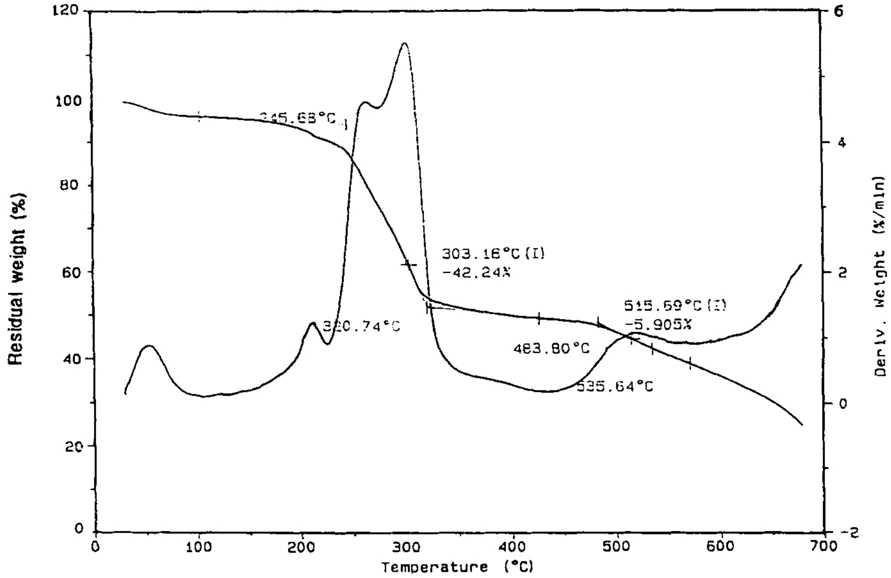


Figure 8. TGA thermogram of poly(TDPA).

TABLE 3. Thermal Stabilities of the Polymer Films from DEDPM and TDPA according to the Temperature[a]

Temp.(°C) Sample (DEDPM/TDPA)	100	200	300	400	500	600	650
100/0	98.46	96.00	85.40	50.93	13.65	1.02	0.84
75/25	97.96	96.94	87.65	43.03	34.30	25.00	14.84
50/50	95.48	93.72	65.12	44.92	38.62	26.76	17.97
25/75	95.65	93.65	68.41	44.97	39.59	32.16	28.07
0/100	95.98	93.37	63.58	44.90	45.27	36.26	26.98

[a]Measured by thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen atmosphere.

nitrogen atmosphere. Figures 6-8 show the TGA thermograms of poly(DEDPM), copolymer (comonomer feed ratio = 1 :1), and poly(TDPA). Figure 5 shows the TCA thermogram of poly(DEDPM) homopolymer. This polymer shows a gradual weight loss after 200°C. The first deriv. weight peak at 400°C is thought to be due to the crosslinking of polyene backbone and the decomposition of polymer. The second deriv. weight peak at 473°C is due to the further decomposition and/or oxidation of char-like residues. Most of the polymer disappeared after the final test temperatue (650°C). On the other hand, in the cases of homopolymer and copolymers having phosphonoacetate functional group (Figures 7-8), the second deriv. weight peak temperature shifted to the higher temperature (at about 520°C) and the peak intensity was also much smaller than that of poly(DEDPM) carrying no phosphonoacetate functional group. Additional thermally stable char materials were formed in the case of the polymer carrying the phosphonoacetate functional group. Table 3 shows the detailed thermogravimetric analysis data of poly(DEDPM), poly(TDPA), and three copolymers. As the feed ratio of TDPA increased in the copolymer, the weight loss at 400°C decreased. On the other hand, the residual weight (char yield) of the polymer above 500°C increased as the feed ratio of TDPA increased. Table 4 shows the electrical conductivity of iodine-doped

TABLE 4. Electrical Conductivity of Iodine-Doped Polymers[a]

Exp. No	Comonomer feed ratio (DEDPM/TDPA)	Composition of I_2-polymer[b]	Electrical conductivity ($\Omega^{-1}cm^{-1}$)[c]
1	100/0	$(C_{13}H_{16}O4)1(I_2)_{0.85}$	2.5×10^{-2}
2	50/50	$(C_{13}H_{16}O_4)_{0.55}(C_{14}H_{21}PO_4)_{0.45}(I_2)_{0.77}$	1.0×10^{-7}
3	0/100	$(C_{14}H_{21}PO_4)_1(I_2)_{0.61}$	7.5×10^{-3}

[a] The polymer film was doped by exposing to the iodine vapor at vacuum (1 mmHg).

[b] The extent of doped iodine was calculated by the weight uptake method.

[c] Measured by the 4-point probe DC method.

poly(DEDPM) and poly(TDPA) homopolymers and copolymer films. The doped iodine contents were in the range of 0.61 and 0.85 per monomeric unit of each polymer. The electrical conductivities of doped polymer films were in the range of 2.5×10^{-2} and 7.5×10^{-3} $\Omega^{-1}cm^{-1}$.

CONCLUSIONS

The cyclocopolymerization of two dipropargyl monomers (DEDPM, TDPA) having different functionalities was carried out. The polymerization by $MoCl_5$ proceeded well to give a high yield of polymer (85-98%). These polymers had a relative high molecular weight ($\overline{Mn}$ = 46000-97000) and soluble in common organic solvents such as chloroform, chlorobenzene, toluene, etc. From the mechanical properties of polymer films, it was found that the tensile properties (tensile strength, modulus, failure strain) decreased as the comonomer feed ratio of TDPA in copolymers increased. Also, it was found that as the feed ratios of TDPA containing phosphonoacetate functional group increased, the char yield at high temperature above 500°C increased.

ACKNOWLEDGEMENT

We gratefully acknowledge support of this research by Kyungpook Sanup University.

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Received September 10, 1996
Revision Received February 20, 1997