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Cyclopolymerization of Diethyl Dipropargylmalonate by Transition-Metal Catalysts

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ABSTRACT: Diethyl dipropargylmalonate was polymerized by $MoCl_5$- and WCl_6-based catalysts to give a new, high molecular weight polymer. A $MoCl_5$-based catalyst was found to be a particularly effective catalyst for cyclopolymerization of diethyl dipropargylmalonate. The number average molecular weight of the resulting polymer was in the range of 76000–127000. The effects of catalysts and solvents on polymerization were also studied. The IR, NMR, and UV–visible spectra of poly(diethyl dipropargylmalonate) supported the idea that the resulting polymer possesses polyene structure having a cyclic recurring unit in the polymer backbone. Poly(diethyl dipropargylmalonate) is a black, soluble, and thermally stable solid.

Introduction

Cyclopolymerization of nonconjugated diynes has been investigated in order to prepare a polymer that contains conjugated double bonds along the polymer backbone and a cyclic recurring unit.[1,2]

Recently, we reported that $MoCl_5$- and WCl_6-based catalyst systems were very effective for the cyclopolymerization of dipropargyl compounds.[3-7] However, there has been no report on the cyclopolymerization of a dipropargyl compound containing an ester group.

In the present paper, we deal with the cyclopolymerization of diethyl dipropargylmalonate (DEDPM) containing ester groups using $MoCl_5$- and WCl_6-based catalysts.

Experimental Section

Preparation of DEDPM.[8] Diethyl malonate (27 g) was added to dry ethanol (150 mL) containing sodium ethoxide (from sodium, 7.8 g). After 5 min, propargyl bromide (42 g) was slowly added to the stirred suspension, and the mixture heated under reflux for 30 min. After removal of the alcohol in a vacuum, the residue was diluted with water, and the neutral fraction was isolated and dissolved in hexane. DEDPM (33 g) slowly separated in octahedra: yield 79%; mp 45.5 °C (lit.[8] mp 45.5 °C).

Other Materials. Tungsten(VI) and molybdenum(V) chloride (Aldrich Chemicals, resublimed, 99+%) were used without further purification. Tetra-*n*-butyltin (Aldrich Chemicals, 99%) and ethyl aluminum dichloride (Aldrich Chemicals, 25% solution in hexane) were used as received. All solvents were purified in the usual manner.

Polymerization. Catalyst preparation and polymerization were carried out under the dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved to make 0.2 M solution in each solvent before use. A typical polymerization procedure is as follows; solvent, catalyst solution, and cocatalyst solution (in case of need) are injected into a 20-mL ampule equipped with a rubber septum in the order given. When a cocatalyst was used, these catalyst systems were aged at 30 °C for 15 min. Finally, monomer in each solvent was injected into the polymerization ampule. After the mixture stood at 60 °C for 24 h, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in chloroform followed by precipitation with a large excess of methanol. The polymer was filtered from the solution and dried to a constant weight under vacuum at 40 °C for 24 h. The polymer yield was calculated by gravimetry.

Instruments for Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian FT-80A spectrometer and a Bruker AM-200 spectrometer, respectively. An infrared spectrum was taken on a Perkin-Elmer 283B spectrometer with a potassium bromide pellet. UV–visible spectra were obtained with a Beckman DU-6 spectrometer. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere at a heating rate of 20 °C/min with a Du Pont 951 TGA. Thermal transitions were measured with a Du Pont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 20 °C/min. Number average molecular weights ($\overline{M}_n$) were determined in THF solution by Waters GPC-150C with a calibration curve for polystyrene standards. Tensile tests were carried out at 20 °C at a strain rate of 86%/min by using Instron 1122; the specimen size was 35 × 10 × 0.2 mm. Electrical con-

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Table I
Polymerization of Diethyl Dipropargylmalonate by Transition-Metal Catalysts[a]

no.	cat. syst[b]	polym yield,[c] %	M_n,[d] × 10^4
1	$MoCl_5$	91	9.7
2	$MoCl_5$-$EtAlCl_2$	75	6.1
3	$MoCl_5$-$(n\text{-}Bu)_4Sn$	95	12.7
4	WCl_6	12	
5	WCl_6-$EtAlCl_2$	10	
6	WCl_6-$(n\text{-}Bu)_4Sn$	15	

[a] Polymerized in 1,4-dioxane at 60 °C for 24 h; $[M]_0 = 0.25$, [Cat.] = [Cocat.] = 5 mM. [b] Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min before used as catalyst. [c] Yields of methanol-insoluble polymers. [d] Determined by GPC with polystyrene standards.

Table II
Polymerization of Diethyl Dipropargylmalonate by $MoCl_5$ in Various Solvents[a]

no.	solvent	polym yield,[b] %
1	chlorobenzene	89[c]
2	cyclohexane	40[c]
3	carbon tetrachloride	90[c]
4	1,2-dichloroethane	43
5	1,4-dioxane	91
6	ethyl acetate	86
7	tetrahydrofuran	43
8	N,N-dimethylformamide	0

[a] Polymerized at 60 °C for 24 h; $[M]_0 = 0.25$, $[MoCl_5] = 5$ mM. [b] Yields of methanol-insoluble polymer. [c] Insoluble polymer in any organic solvents.

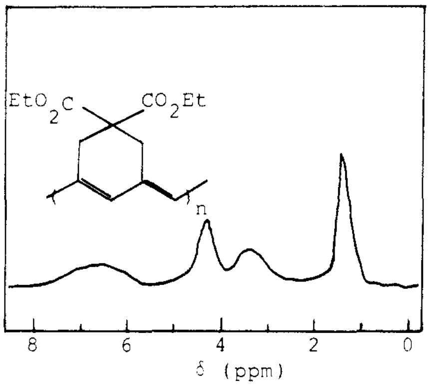

Figure 1. ^1H NMR spectrum of poly(diethyl dipropargylmalonate) (sample: Table I, no. 3, measured in $CDCl_3$).

ductivity was measured by a 2-point probe dc method with a Hewlett-Packard 6216 A power supply and a Keithley 485 picoammeter.

Results and Discussion

The polymerization of DEDPM was carried out in the presence of transition-metal catalysts under various reaction conditions.

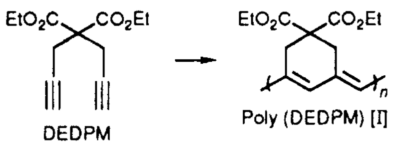

Table I lists the results of the polymerization of DEDPM by using $MoCl_5$- and WCl_6-based catalysts. $MoCl_5$ alone polymerized DEDPM very effectively. $(n\text{-}Bu)_4Sn$ has been known to be an excellent cocatalyst for the polymerization of mono- and disubstituted acetylenes.[3,5,9-11] However, as shown in Table I, $(n\text{-}Bu)_4Sn$ hardly affected the polymer yield but increased the number average molecular weight ($\overline{M}_n$). On the other hand, $EtAlCl_2$ decreased polymer yield as well as M_n. WCl_6 exhibited markedly less effective catalytic activity than $MoCl_5$. As a cocatalyst of WCl_6, neither $(n\text{-}Bu)_4Sn$ nor $EtAlCl_2$ had any effect on the polymerization reaction. $MoCl_5$-$(n\text{-}Bu)_4Sn$ as a catalyst system resulted in the highest polymer yield (95%) and M_n (127 100), which is consistent with the cyclopolymerization of dipropargylcarbinol.[6]

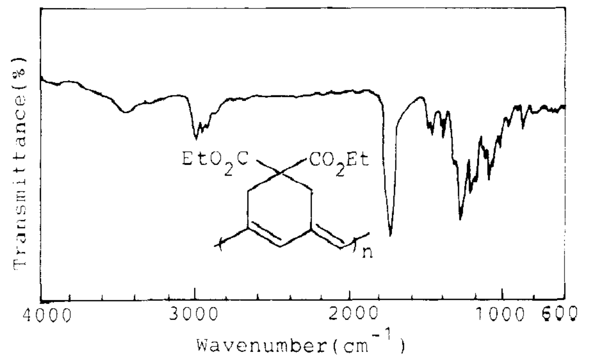

Figure 2. IR spectrum of poly(diethyl dipropargylmalonate) (sample: Table I, no. 3, KBr pellet).

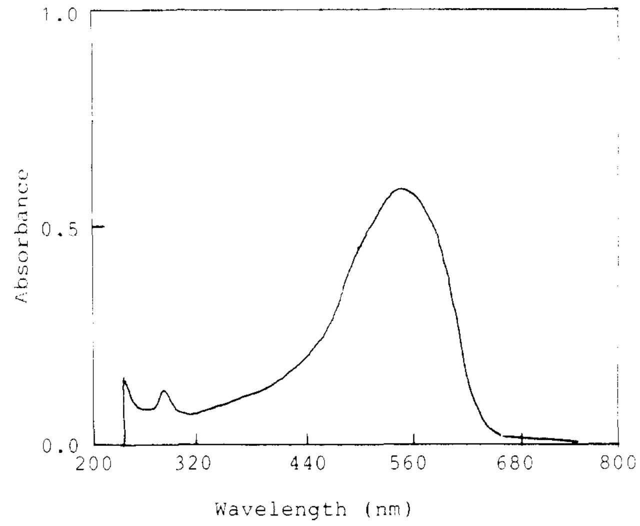

Figure 3. UV–visible spectrum of poly(diethyl dipropargylmalonate) (sample: Table I, no. 3, measured in THF).

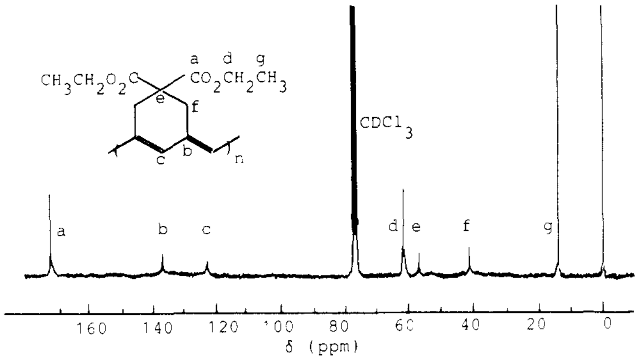

Figure 4. ^{13}C NMR spectrum of poly(diethyl dipropargylmalonate) (sample: Table I, no. 3, measured in $CDCl_3$).

Polymerization of DEDPM in various solvents was investigated to study the solvent effect on the polymerization. As shown in Table II, poly(DEDPM) was obtained in fair yields in various solvents such as chlorobenzene, carbon tetrachloride, 1,4-dioxane, and ethyl acetate. Chlorobenzene, carbon tetrachloride, and cyclohexane, however, gave insoluble polymers. These results are similar to those reported for the polymerization of propiolic acid

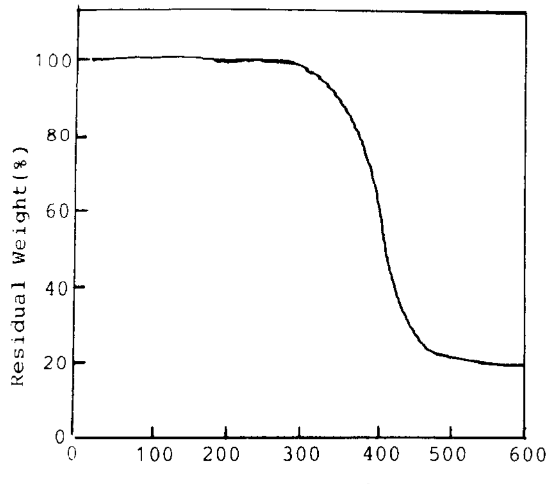

Figure 5. TGA curve of poly(diethyl dipropargylmalonate) (sample: Table I, no. 3).

derivatives.[9]

The polymer structure was identified by (^{1}H and ^{13}C) NMR, IR, and UV-visible spectroscopies. Figure 1 represents the ^{1}H NMR spectrum of poly(DEDPM). At 5.5–8 ppm appeared the new peak, which is assigned to the protons on the conjugated double bonds. Figure 2 shows the IR spectrum of poly(DEDPM). No acetylenic carbon–hydrogen stretching band (3310 cm^{-1}) was found in the IR spectrum of poly(DEDPM). The UV-visible spectrum of the polymer was obtained in THF (Figure 3). The spectrum of the polymer exhibits a characteristic broad peak of 300–600 nm that is due to a π–π^* transition of conjugated polyene. In the ^{13}C NMR spectrum (Figure 4), two peaks at 123 and 137 ppm are assigned to the conjugated double bond and a peak at 172 ppm is due to the carbonyl carbon.

The resulting polymer is easily soluble in chloroform, 1,4-dioxane, ethyl acetate, THF, and DMF. It is, however, insoluble in *n*-hexane, toluene, ethyl ether, and methanol. A black uniform film was easily obtained by casting the polymer solution in chloroform on a glass plate. Thus, spectral data obtained as above and solubility behavior lead to a conclusion that the structure I could be the most favorable one for the resulting polymer.

The TGA thermogram of poly(DEDPM) under nitrogen atmosphere (Figure 5) shows that poly(DEDPM) is thermally stable up to 290 °C and degrades at temperatures above 290 °C. The DSC curve shows two irreversible exothermic processes, one peaking at 138 °C and the other at 280 °C (Figure 6). This behavior at 138 °C is attributed to the rearrangement of the exo double bond of poly(DEDPM), converting the polymer from a helical structure to a nearly planar polyene backbone configuration. This process may be compared to poly(1,6-heptadiyne)[2] and poly(dipropargyl sulfide)[3] at 107 and 160 °C, respectively. The following mechanical properties were obtained with tensile measurement at a constant rate of stretching of 86%/min at 20 °C: Young's modulus (E) 4800 MPa; tensile strength (σ_B) 104 MPa; ultimate elongation (γ_B) 3.4%.

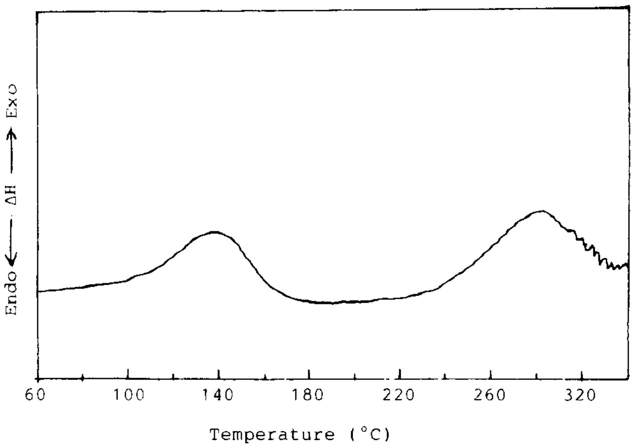

Figure 6. DSC curve of poly(diethyl dipropargylmalonate) (sample: Table I, no. 3).

The electrical conductivity of poly(DEDPM) film at 25 °C was 3.5×10^{-11} S cm^{-1}. We are now attempting to increase electrical conductivity by various doping methods.

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Registry No. I (homopolymer), 40921-05-9; I (SRU), 126615-62-1; $MoCl_5$, 10241-05-1; $EtAlCl_2$, 563-43-9; (n-Bu)$_4$Sn, 1461-25-2; WCl_6, 13283-01-7.