Catalytic Cyclopolymerization and Copolymerization of Diethyl Dipropargylmalonate by (toluene)Mo(CO)₃

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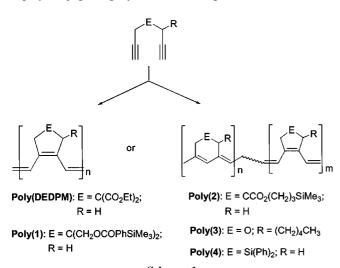
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Catalytic copolymerization of diethyl dipropargylmalonate (DEDPM) and phenylacetylene (PA) by Mo(CO)₆ and (toluene)Mo(CO)₃/chloranil has resulted in the expected copolymer consiting of a polyene backbone with five- and/or six-membered rings and the PPA structure. Both complexes exhibited not only varying degree of catalytic activity depending upon the relative mole ratio of two monomers but also characterize the types of coploymers. The former yields the polyene backbone containing only five-membered rings as well as PA while the latter produces the polymers consisting of both five- and six-membered ring structure. Comparative studies show that Mo(CO)₆ exhibits reactivity toward DEDPM alone, thus catalyzing initially metathesis cyclopolymerization of DEDPM followed by copolymerization with PA while the (toluene)Mo(CO)₃/chloranil system shows affinity for both PA and DEDPM.

Introduction

During the past two decades odd-electron organometallic species have gained an increasing realization in stoichiometric and catalytic transformations.[1] The observed large enhancement in the reaction rate upon oxidation or reduction of the respective 18-electron metal complexes and further amplification of this activation process are the basis for now well-established electron-transfer-chain (ETC) catalysis that calls for, in principle, partial (*not stoichiometric*) oxidation of the metal complexes.[2] Metal-centered radicals, thus generated in a chain-transfer mechanism, have been put to use in a variety of synthetically useful transformations, such as CO insertion, ligand substitution, and polymerization.[3-5]

We have recently shown that Mo(CO)₆ can catalyze very effectively metathesis polymerization of a series of 1,6-heptadiynes to give corresponding poly(1,6-heptadiynes) with highly conjugated polyenes under simple thermal conditions (Scheme 1).[6,7]
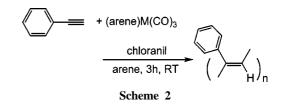
Other group had shown earlier that (arene)M(CO)₆ complexes (M = Cr, Mo, or W; arene = toluene, *o*-xylene, or mesitylene) can also be successfully employed as catalyst for the polymerization of terminal alkynes like phenylacetylene (PA) under thermal as well as ETC catalytic conditions.[5c-e, 8] Further, this same group has found that addition of 1 equiv of chloranil to a solution containing an equimolar amount of the (toluene)MO(CO)₃ complex and 50 equiv of the monomer, PA, induces rapid polymerization at ambient conditions to give a near quantitative yield of polyphenylacetylene (PPA) (Scheme 2).

These findings and our success of high yield synthesis of poly(1,6-heptadiynes) by Mo(CO)₆ have prompted us to attempt the synthesis of a copolymer containing both 1,6-hepatadiynes and PA. The motivation behind this effort is the fact that PPA is already well known for its electrical and optical properties such as third-order nonlinear optical properties.[9-12] In addition PA is frequently incorporated to increase solubility and processability of the polymer.[13] Thus our poly(1,6-heptadiynes) which are readily soluble in most organic solvents, once incorporated into the copolymer containing PPA would make the job much easier.

In this paper, we wish to report the cyclopolymerization and copolymerization of diethyl dipropargylmalonate (DEDPM) with PA catalyzed by the chloranil/(toluene)Mo(CO)₆ catalyst under various reaction conditions. Catalysis by Mo(CO)₆ has also been carried out for comparative purposes.

Poly(DEDPM): E = C(CO₂Et)₂;
      R = H

Poly(1): E = C(CH₂OCOPhSiMe₃)₂;
      R = H

Poly(2): E = CCO₂(CH₂)₃SiMe₃;
      R = H

Poly(3): E = O; R = (CH₂)₄CH₃

Poly(4): E = Si(Ph)₂; R = H

Scheme 1

Scheme 2

Experimental Section

Materials. Mo(CO)$_6$ (Aldrich) was sublimed prior to use. Phenyl acetylene (Aldrich) was distilled over calcium hydride before use. All solvents were used after purification according to conventional methods. (toluene)Mo(CO)$_3$[14] and diethyl dipropargylmalonate (DEDPM)[15] were prepared according to the literature procedures.

Characterization. NMR spectra were recorded on a Varian Unity Inova 300 WB Spectrometer operating at 300 MHz (^{1}H), 75.5 MHz (^{13}C), and 59.6 MHz (^{29}Si), respectively. FT-IR spectra were measured as KBr pellets on a Mattson FT-IR Galaxy 7000 series Spectrophotometer. UV-Visible spectra were obtained in CH$_2$Cl$_2$ on a Shimazu UV-2100 Spectrophotometer. Molecular weights were determined in CH$_2$Cl$_2$ solution by TSP P-1000 apparatus containing Shodex KF-800 series columns and Shodex RI-71 detector with a calibration curve for polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Rheometric STA 1500 under nitrogen atmosphere with a heating rate of 10 ºC/min in the temperature range of 20-800 ºC and 20-400 ºC, respectively.

Copolymerization of DEDPM and PA by Mo(CO)$_6$. DEDPM (1.17 g, 5 mmol) and Mo(CO)$_6$ (0.17 g, 0.1 mmol) were taken in 20 mL of 1,4-dioxane in a dry 100 mL flask fitted with a nitrogen inlet and a stirring bar, and an appropriate amount of PA was added by syringe. The solution was stirred for 48 h at 100 ºC. The polymer was precipitated by adding 50 mL of methanol, filtered, washed with methanol several times, and vacuum-dried to constant weight. ^{1}H NMR (CDCl$_3$) δ 1.2-1.3 (br, -CH$_3$), 2.5-3.5 (br, ring CH$_2$), 4.21-4.25 (br, -OCH$_2$), 6.0-8.0 (br, phenyl, HC=C).

Copolymerization of DEDPM and PA by (toluene)-Mo(CO)$_3$/chloranil. DEDPM (5 mmol) and an appropriate amount of PA were taken in a dry 100 mL flask fitted with a nitrogen inlet and a magnetic stirrer, and (toluene)Mo(CO)$_3$ (0.0278 g, 0.1 mmol) in 10 mL of toluene was added by syringe. Chloranil (0.0045 g, 0.1 mmol) dissolved in 10 mL of toluene was added to the flask by syringe. The solution was stirred at room temperature for 6 h during which the color of the solution was turned to deep purple. The polymer was precipitated by adding methanol (50 mL) and filtered on a glass filter. This was washed with methanol several times and vacuum-dried to constant weight. ^{1}H NMR (CDCl$_3$) δ 1.16-1.26 (br, -CH$_3$), 2.5-3.6 (br, ring CH$_2$), 4.10-4.27 (br, -OCH$_2$), 5.6-8 (br, phenyl, HC=C).

Results and Discussion

Copolymerization of DEDPM and PA. Table 1 shows the results of copolymerization of DEDPM and PA catalyzed by Mo(CO)$_6$ and (toluene)Mo(CO)$_3$/chloranil. The table shows that PA alone, where X = 0, is totally unreactive toward the action of Mo(CO)$_6$ under the reaction conditions employed for the synthesis of poly(1,6-heptadiynes). These observations are quite contrasting with those found with rhodium(I) complexes of the type [(diene)Rh(LL)]A (LL =

Table 1. Copolymerization of DEDPM and PA

X$_{DEDPM}$[a]	Catalyst[b]	M_w	M_n	PDI	Yield (%)	λ_{max} (nm)
1	A	185,000	110,000	1.68	94	548
	B	93,000	75,000	1.24	50	546
0.75	A	37,000	27,000	1.37	40	516
	B	75,000	58,000	1.30	35	484
0.50	A	16,000	10,500	1.51	30	442
	B	50,000	36,000	1.36	30	422
0.25	A	8,500	4,700	1.76	8	246
	B	67,000	48,000	1.40	30	394
0	A	–	–	–	–	–
	B	76,000	54,000	1.41	97	250

[a]Mole fraction of DEDPM in the mixture of DEDPM and PA. [b]Catalysis A: polymerized at 100 ºC for 48 h in 1,4-dioxane; [monomer]$_o$ = 5 mmol; [Mo(CO)$_6$] = 0.1 mmol. Catalysis B: Polymerized at RT for 6 h in toluene; [monomer]$_o$ = 5 mmol; [(toluene)Mo(CO)$_6$/chloranil] = 0.1 mmol /0.1 mmol.
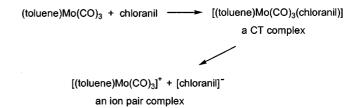
dinitrogen chelating ligand; A = ClO$_4^-$, PF$_6^-$) which are well-known catalysts for the polymerization of PA.[16,17]

Although (toluene)Mo(CO)$_3$ alone is incapable of inducing the polymerization of PA, addition of 1 equivalent of chloranil to a solution containing an equimolar amount of the (toluene)Mo(CO)$_3$ induces rapid copolymerization as well as polymerization of PA thus making the reaction go to completion in 6 h at room temperature. The observed large enhancement in the reaction rate may be explained in terms of at least two key stpes in the reaction, *viz.* electron-transfer and polymerization by metathesis as illustrated in Scheme 3.
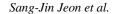
According to this scheme, the formation of a transient CT complex between (toluene)Mo(CO)$_3$ and the acceptor chloranil apparently promotes a fast-electron-transfer process, generating a 17-electron (toluene)Mo(CO)$_3$ complex, an odd-electron species. The formation of this complex is now well-evidenced in the literature.[5e]
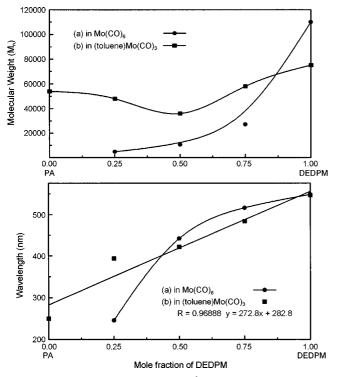
The 17-electron [(toluene)Mo(CO)$_3$]$^+$ complex which is substitutionally labile, would accommodate a molecule of terminal alkyne aided possibly by the ring-slipping of the arene ligand while initiation of polymerization by metathesis could be preceded by the now well-established η^2-alkyne-vinylidene rearrangement route.[18]

The remaining feature of Table 1 is that the relative amount of DEDPM and PA affects both molecular weight (M_n) and λ_{max} values of the polymer products. Thus, as illustrated in Figure 1, both the Mo(CO)$_6$ and (toluene)Mo(CO)$_3$/chloranil catalyses show qualitative dependence of both M_n and λ_{max} upon the mole fraction of DEDPM. The slight dif-

(toluene)Mo(CO)$_3$ + chloranil $\longrightarrow$ [(toluene)Mo(CO)$_3$(chloranil)]

a CT complex

[(toluene)Mo(CO)$_3$]$^+$ + [chloranil]$^-$

an ion pair complex

Scheme 3

Figure 1. Dependence of M_n (top) and λ_{max} (bottom) on the Relative Amount of Monomers.

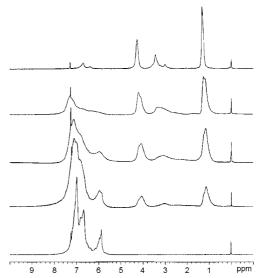**Table 2**. The Relationship between Feed ratio and Product ratio

Feed ratio[a]	Catalyst system[b]	Product ratio[c]
DEDPM : PA		DEDPM : PA
3 : 1	A	3 : 0.6
	B	3 : 2
1 : 1	A	1 : 0.5
	B	1 : 2
1 : 3	A	1 : 1.6
	B	1 : 4.4

[a]Initial mole ratios of two monomers. [b]Catalyst system A = $Mo(CO)_6$; B = (touluene)$Mo(CO)_3$/chloranil. [c]Determined by ^1H NMR.

ference between two catalytic systems is that greater reactivity toward DEDPM is observed with the $Mo(CO)_6$ catalysis. Thus $Mo(CO)_6$ catalyzes initially metathesis cyclopolymerization of DEDPM, which is followed by copolymerization with PA. With (toluene)$Mo(CO)_3$/chloranil system, however, polymerization of PA is initiated first.

The results listed in Table 2 are in agreement with the above statement. It can be seen that relative numbers of each of copolymer depend upon both the relative amount of monomers and the types of catalysts. Again, as expected, the percentage of PA in the product is higher than the feed ratio in the reaction mixture when the (toluene)$Mo(CO)_3$/chloranil system is employed as catalyst, while the opposite is true with $Mo(CO)_6$ exhibiting approximately only half an amount of the PA as expected in the product.

The product formation was confirmed by GPC, ^1H NMR, and IR spectroscopy. First of all, the formation of copoly-

Figure 2. ^1H NMR Spectra (from top to bottom) of poly(DEDPM) ($X_{DEDPM} = 1$); copolymers ($X_{DEDPM} = 0.75, 0.5, 0.25$ with descending order); PPA ($X_{DEDPM} = 0$).

mers was confirmed by their GPC bands consisting of unimodal curves for all cases. Figure 2 shows ^1H NMR spectra of pure poly(DEDPM) (Figure 2(A)), copolymers of PA and DEDPM (Figs. 2(B)-(D)), and pure PPA (Figure 2(E)) obtained by the (toluene)$Mo(CO)_3$/chloranil catalyst. As can be deduced from Table 2, intensity of the signal due to the PA unit, *i.e.*, the broad phenyl signal at around 7 ppm, grows with increase in the mole fraction of PA.

Careful analysis of ^1H and ^{13}C NMR spectra of poly-(DEDPM) and other copolymers obtained from the (toluene)$Mo(CO)_3$/chloranil catalyst along with our previous
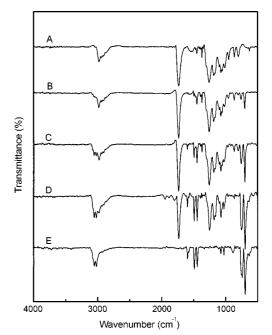

Figure 3. IR Spectra of (A) poly(DEDPM) ($X_{DEDPM} = 1$); (B)-(D) copolymers with $X_{DEDPM} = 0.75$, $X_{DEDPM} = 0.5$, $X_{DEDPM} = 0.25$; (E) PPA ($X_{DEDPM} = 0$).
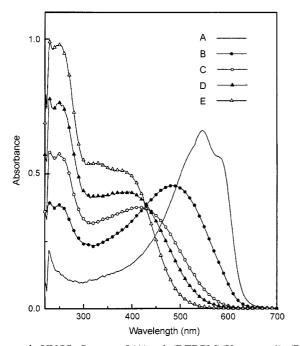
Figure 4. UV/Vis Spectra of (A) poly(DEDPM)($X_{DEDPM} = 1$); (B)-(D) copolymers with $X_{DEDPM} = 0.75$, $X_{DEDPM} = 0.5$, $X_{DEDPM} = 0.25$; (E) PPA with $X_{DEDPM} = 0$.

Figure 5. TGA thermograms of (A) poly(DEDPM)($X_{DEDPM} = 1$); (B)-(D) copolymers with $X_{DEDPM} = 0.75$, $X_{DEDPM} = 0.5$, $X_{DEDPM} = 0.25$; (E) PPA with $X_{DEDPM} = 0$.

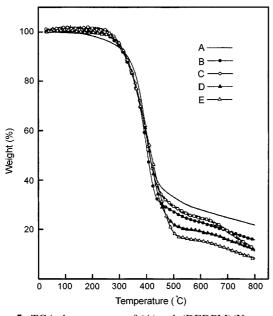results with related polymers[6,7] allowed us to confirm that this system, unlike $Mo(CO)_6$, produces the polymers consisting of both five- and six-membered ring structures in the polymer backbone as shown in Scheme 1.

The IR spectra of these polymers are consistent with these observations (Figure 3). The intense band at 700 cm^{-1} and a pair of bands at 760-740 cm^{-1}, which are characteristic bands of *cis*-PPA, are growing as the mole fraction of PA is increased.

In agreement with these observations, UV-Visible spectra of copolymers (Figure 4) show not only the growing of the characteristic band of PA (the band below 300 nm) but the hypsochromic shift (blue shift) of the band for $\pi^* \leftarrow \pi$ transition with increase in the mole fraction of PA. This blue shift may be explained in terms of limited conjugation due to the linearly twisted structure of PA.

Thermal properties of the copolymers are similar to those of poly(DEDPM) and do not vary significantly regardless of the mole ratio of PA or DEDPM in the polymer backbone as shown in Figure 5. They are stable up to 300 °C, and total decompositions occur between 300 °C and 800 °C with rapid decomposition rate in the range of 300-480 °C, then the residuals reach 10-20% at 800 °C.

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