Polymerization of propiolic acid and its derivatives catalysed by $MoCl_5$

Toshio Masuda, Michio Kawai and Toshinobu Higashimura
Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan
(Received 9 June 1981; revised 8 July 1981)

The polymerization of propiolic acid by group VI and VIII transition metal catalysts was investigated. $MoCl_5$, which was the most active among the catalysts examined, provided poly(propiolic acid) in over 80% yields under favourable conditions. The polymer formed was a water-soluble tawny powder, and its molecular weight was low (η_{sp}/C 0.04–0.05 dl g^{-1}). The polymer structure, $\{CH=C(CO_2H)\}_n$ was confirmed by the i.r. and ^{13}C n.m.r. spectra and elemental composition. Some derivatives of propiolic acid (methyl propiolate, acetylenedicarboxylic acid, and phenylpropiolic acid) also produced coloured powdery polymers in the presence of $MoCl_5$-based catalysts.

Keywords Polymerization; propiolic acid; transition metal catalysts; powdery polymers; structure

INTRODUCTION

The polymerizations of propiolic acid ($HC\equiv CCO_2H$) induced by heat, light, and radiation have been attempted[1,2]. The polymer yields, however, were as low as 10–30%, and the molecular weights of resultant polymers were less than 2000. Further, the elemental compositions of the polymers were appreciably different from the theoretical one, which was attributed to decarboxylation and dehydration of polymers.

Catalytic polymerization of propiolic acid has not been reported so far. To our knowledge, there have been no reports on the polymerization of phenylpropiolic acid ($C_6H_5C\equiv CCO_2H$), either. Thiese might be associated with the fact that propiolic acids are not polymerized by Ziegler-type catalysts which are effective for the polymerization of acetylenic hydrocarbons.

Catalysts based on $MoCl_5$ and WCl_6 are capable of polymerizing both aromatic and aliphatic acetylene derivatives[3,4]. This polymerization proceeds not only in aromatic and halogenated hydrocarbons but also in oxygen-containing solvents such as ethers, esters and ketones[5]. This suggests that propiolic acid, an oxygen-containing acetylenic monomer, can be polymerized by $MoCl_5$- and WCl_6-based catalysts. Unlike hydrocarbon monomers, propiolic acid will produce a hydrophilic polymer and hence interesting functionalities are expected for the polymer.

In this paper, we report on the polymerization of propiolic acid catalysed by $MoCl_5$. The polymerizations of some derivatives of propiolic acid were also examined.

EXPERIMENTAL

Propiolic acid (Tokyo Chemical Industry Co., purity >95%) was distilled under reduced pressure. Phenylpropiolic acid (Aldrich Chemical Co., purity 97%) was dried under reduced pressure at room temperature over phosphorus pentoxide. Methyl propiolate, acetylenedicarboxylic acid and acetylenedicarboxylic acid dimethyl ester (Tokyo Chemical Industry Co., purities >98%) were used as received.

Polymerization was carried out under a dry nitrogen atmosphere at 60°C for 24 h in solution unless otherwise stated. In the case where a cocatalyst was used for polymerization, a 1:1 mixture of $MoCl_5$ and a cocatalyst in solution was aged at 60°C for 15 min before use. The polymerization of acid monomers (propiolic acid, acetylenedicarboxylic acid, and phenylpropiolic acid) was terminated by the addition of a small amount of methanol. The polymers formed were isolated by precipitation in a large amount of hexane, and purified by reprecipitation from a tetrahydrofuran solution into a 1:4 mixture of diethyl ether and hexane. However, the polymerization of ester monomers (methyl propiolate and acetylenedicarboxylic acid dimethyl ester) was terminated by pouring the reaction mixture into a large amount of methanol. All the polymers precipitated were filtered off and dried under reduced pressure. Polymer yields were determined by means of gravimetry.

Reduced viscosities, η_{sp}/C, were measured at 30°C in ethanol [poly(propiolic acid) and poly(acetylenedicarboxylic acid)], 1,4-dioxane [poly(methyl propiolate)] or butan-2-one [poly(phenylpropiolic acid)] (concn. 1.0 g dl^{-1}). I.r. spectra were recorded on a Shimadzu IR27G spectrophotometer. Thermal gravimetrical analysis was conducted with a Shimadzu 20B analyser under nitrogen. ^{13}C n.m.r. spectra were observed in $(CD_3)_2SO$ solution (20% w/v) on a JNM FX90Q spectrometer.

RESULTS AND DISCUSSION

Polymerization of propiolic acid

Table 1 lists the results for the polymerization of propiolic acid by group VI and VIII transition metal chlorides. $MoCl_5$ polymerized propiolic acid effectively; i.e., the polymer yield reached ~80% when the polymerization was carried out in 1,4-dioxane. However,

0032-3861/82/050744-04$03.00

Table 1 Polymerization of propiolic acid by transition metal chloride-based catalysts*

No.	Catalyst	Solvent	Yield (%)
1	$MoCl_5$	1,4-Dioxane	81
2	$MoCl_5 \cdot Ph_4Sn$	"	84
3	$MoCl_5 \cdot Ph_3Sb$	"	83
4	WCl_6	"	0
5	$WCl_6 \cdot Ph_4Sn$	"	0
6	$WCl_6 \cdot Ph_3Sb$	"	0
7	$RuCl_3 \cdot 3H_2O$	Ethanol	11
8	$RhCl_3 \cdot 3H_2O$	"	12
9	$PdCl_2$	"	36

* Polymerized at 60°C for 24 h; $[M]_0 = 1.0$ mol l^{-1}, [Cat] = 30 mmol l^{-1}

Table 2 Polymerization of propiolic acid by $MoCl_5$ in various solvents*

No.	Solvent	Yield (%)	η_{sp}/C† (dl g^{-1})
1	1,4-Dioxane	60	0.047
2	Ethyl acetate	34	0.039
3	1,2-Dimethoxyethane	27	0.041
4	Acetic acid	10	0.042
5	Toluene	8	–
6	Anisole	4	–
7	1,2-Dichloroethane	3	–
8	Acetonitrile	3	–
9	n-Butyl ether	0	–
10	Butan-2-one	0	–

* Polymerized at 60°C for 24 h; $[M]_0 = 3.0$ mol l^{-1}, [Cat] = 30 mmol l^{-1}
† Measured in ethanol at 30°C (concn. 1.0 g dl^{-1})

WCl_6 was completely ineffective. This finding is interesting as compared with those for other monomers; WCl_6 is more active than $MoCl_5$ in the polymerization of phenylacetylene[3], and these catalysts show comparable activities in the polymerization of tert-butylacetylene[4].

It is known that the addition of small amounts of reducing agents such as Ph_4Sn increases the yields in the WCl_6-catalysed polymerizations of phenylacetylene[6], 1-phenyl-1-propyne[7] and diphenylacetylene[8]. *Table 1*, however, shows that Ph_4Sn and Ph_3Sb hardly affected the yields in both $MoCl_5$ and WCl_6 catalysed polymerizations. Thus, $MoCl_5$ exhibits high catalyst activity by itself in the polymerization of propiolic acid.

Group VIII transition metal catalysts are capable of polymerizing not only acetylenic hydrocarbons such as phenylacetylene[9], but also polar group containing acetylenes like acetylenic alcohols[10,11]. Therefore it is interesting to study the polymerization of propiolic acid by group VIII transition metal catalysts. Polymerization was attempted using $RuCl_3 \cdot 3H_2O$, $RhCl_3 \cdot 3H_2O$, and $PdCl_2$ as catalysts. Ethanol was used as solvent since it was a good solvent for both catalysts and the monomer. As a consequence, polymer yields were 10–40% (see *Table 1*, Nos. 7–9). It was, however, difficult to remove the catalyst residue completely because even after termination of polymerization group VIII catalyst metals remained coordinated to the conjugated double bonds of polymer formed.

As *Table 2* shows, poly(propiolic acid) was obtained in fair yields in 1,4-dioxane, ethyl acetate, and 1,2-dimethoxyethane with $MoCl_5$ at 60°C. These solvents seem to satisfy the following requirements: (i) retention of the $MoCl_5$ activity (inertness to $MoCl_5$), and (ii) high dissolving ability for poly(propiolic acid). In acetic acid, acetonitrile, and butan-2-one, the polymer yields were not more than 10%, probably because these solvents did not fulfil the former condition. However, the reason that toluene, anisole, 1,2-dichloroethane, and *n*-butyl ether are not favourable as polymerization solvents seems to be that they do not meet the latter requirement. The reduced viscosity of polymers hardly depended on the kind of solvent.

Figure 1 shows the time dependences of polymer yield and viscosity in the polymerization of propiolic acid. Polymer yield reached ~60% after 1 day and levelled off. This polymerization did not proceed when as much poly(propiolic acid) as in the feed monomer had been added beforehand. Therefore, the limit observed for polymer yield is due to the inhibition of polymerization by the polymer formed. The reduced viscosity of polymer was ~0.045 dl g^{-1} irrespective of conversion.

The polymerization did not occur at 30°C, while the yields at 60° and 90°C were comparable (*Table 3*, Nos. 1–3). Polymer yield increased with decreasing monomer concentration (*Table 3*, Nos. 2, 4 and 5) and with increasing catalyst concentration (*Table 3*, Nos. 2, 6 and 7). Polymer viscosity hardly depended on these polymerization conditions.

The above results on propiolic acid polymerization lead to a conclusion that propiolic acid, an acetylene having a polar functional group, can be polymerized by $MoCl_5$. Further, the reduced viscosity of ~0.045 dl g^{-1} for the poly(propiolic acid) formed, suggests that the polymer molecular weight is similar to or somewhat greater than the value of 2000 reported in the literature[2].

Polymerization of derivatives of propiolic acid

The polymerization of some derivatives of propiolic acid was studied (*Table 4*). Methyl propiolate produced a polymer in ~30% yields, which are lower than these (~80%) for propiolic acid under the same conditions. Acetylenedicarboxylic acid gave a polymer in a low yield with $MoCl_5 \cdot Ph_4Sn$, while acetylenedicarboxylic acid dimethyl ester underwent no polymerization. Thus the acid monomers were more reactive than the corresponding ester monomers, and the monosubstituted

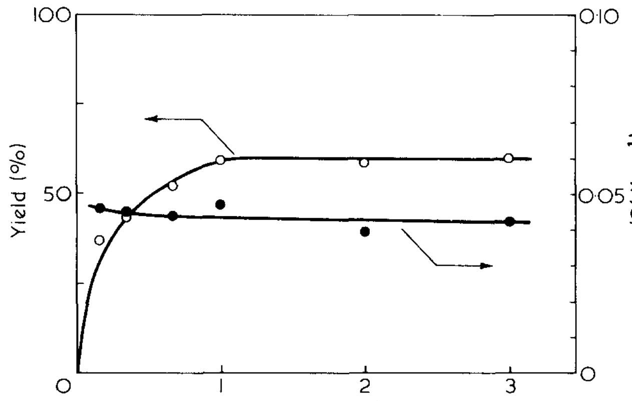

Figure 1 Time dependences of yield and reduced viscosity for the polymerization of propiolic acid by $MoCl_5$ in 1,4-dioxane at 60°C; $[M]_0 = 3.0$ mol l^{-1}, [cat] = 30 mmol l^{-1}

Table 3 Effects of temperature, monomer and catalyst concentrations on the polymerization of propiolic acid*

No.	Temperature (°C)	$[M]_0$ (mol l^{-1})	$[MoCl_5]$ (mmol l^{-1})	Yield (%)	η_{sp}/C† (dl g^{-1})
1	30	3.0	30	0	–
2	60	3.0	30	60	0.047
3	90	3.0	30	60	0.046
4	60	1.0	30	81	0.040
5	60	5.0	30	50	0.045
6	60	3.0	10	35	0.044
7	60	3.0	20	46	0.047

* Polymerized in 1,4-dioxane for 24 h
† Measured in ethanol at 30°C (concn. 1.0 g dl^{-1})

Table 4 Polymerization of derivatives of propiolic acid by $MoCl_5$ and $MoCl_5 \cdot Ph_4Sn$*

No.	Monomer	Catalyst	Yield (%)	η_{sp}/C† (dl g^{-1})
1	$H{-}C{\equiv}C{-}CO_2CH_3$	$MoCl_5$	27	0.062
2	"	$MoCl_5 \cdot Ph_4Sn$	31	0.063
3	$HO_2C{-}C{\equiv}C{-}CO_2H$	$MoCl_5$	0	–
4	"	$MoCl_5 \cdot Ph_4Sn$	13	0.026
5	$H_3CO_2C{-}C{\equiv}C{-}CO_2CH_3$	$MoCl_5$	0	–
6	"	$MoCl_5 \cdot Ph_4Sn$	0	–

* Polymerized in 1,4-dioxane at 60°C for 24 h; $[M]_0$ = 1.0 mol l^{-1} (Nos. 3, 4: 0.050 mol l^{-1}), [Cat] = 30 mmol l^{-1}
† Measured in 1,4-dioxane (Nos. 1, 2) or in ethanol (No. 4) at 30°C (concn. 1.0 g dl^{-1})

Table 5 Polymerization of phenylpropiolic acid by $MoCl_5$- and WCl_6-based catalysts*

Catalyst	Solvent	Yield (%)	η_{sp}/C† (dl g^{-1})
$MoCl_5$	1,4-Dioxane	25	0.040
$MoCl_5 \cdot Ph_4Sn$	"	38	0.038
$MoCl_5 \cdot Bu_4Sn$	"	43	0.037
$MoCl_5 \cdot Ph_3Sb$	"	48	0.037
WCl_6	"	0	–
$WCl_6 \cdot Ph_4Sn$	"	0	–
$MoCl_5 \cdot Ph_4Sn$	Ethyl acetate	18	0.037
"	Toluene	5	–
"	1,2-Dichloroethane	10	–

* Polymerized at 60°C for 24 h; $[M]_0$/[Cat] = 100/3, $[M]_0$ = 1.0 mol l^{-1} (No. 8, 0.3; No. 9, 0.5)
† Measured in butan-2-one at 30°C (concn. 1.0 g dl^{-1})

monomers than the corresponding disubstituted monomers: $HC{\equiv}CCO_2H$ > $HC{\equiv}CCO_2CH_3$ > $HO_2CC{\equiv}CCO_2H$ > $H_3CO_2CC{\equiv}CCO_2CH_3$.

Phenylpropiolic acid, which is another disubstituted acetylene derived from propiolic acid, was polymerized in fairly high yields by $MoCl_5$-based catalysts, so that the polymerization of this monomer was examined in some detail (see *Table 5*). Though $MoCl_5$ provided poly(phenylpropiolic acid) without a cocatalyst, the use of Ph_4Sn, Bu_4Sn and Ph_3Sb as cocatalysts appreciably enhanced the yield. As in the case of propiolic acid, WCl_6 exhibited no catalytic activity in the absence and presence of Ph_4Sn. 1,4-Dioxane attained the highest yield among the solvents examined. The polymer formed in 1,4-dioxane contained an insoluble fraction (~40%), while those obtained in other solvents were completely soluble in appropriate solvents. Polymer viscosity was about 0.040 dl g^{-1} regardless of the kinds of cocatalyst and solvent.

Properties and structure of polymers

The data for the elemental analysis of poly(propiolic acid) are as follows: *Table 2*, sample No. 1) $(C_3H_2O_2)_n$; calculated: C, 51.42; H, 2.87; O, 45.71; found: C, 50.31; H, 3.87; O, 45.82. The values found do not agree well with the theoretical values, which is attributed to the decarboxylation reaction and moisture absorption of polymer. These values, however, are much better than those for the polymer obtained by thermal polymerization at 200°C (C, 60.35; H, 3.09; O, 36.70)[1]. On the other hand, the values for the analysis of poly(methyl propiolate) practically coincided with the theoretical values: (sample from *Table 4*, No. 2) $(C_4H_4O_2)_n$; calculated: C, 57.14; H, 4.80; O, 38.06; found: C, 56.88; H, 4.88; O, 38.23. The absence of free carboxyl groups in the polymer seems responsible for this good agreement.

Poly(propiolic acid) was a tawny powder. Poly(methyl propiolate), poly(acetylenedicarboxylic acid), and poly(phenylpropiolic acid) were greyish white, grey, and yellow powders, respectively. Poly(propiolic acid) and poly(acetylenedicarboxylic acid) were soluble in highly polar solvents such as water and methanol, and insoluble in less polar solvents like benzene and chloroform. In contrast to this, poly(methyl propiolate) was soluble in benzene and chloroform, while insoluble in water and methanol. Poly(phenylpropiolic acid) dissolved in moderately polar solvents such as butan-2-one, dimethylsulphoxide, and ethanol. As described above, however, poly(phenylpropiolic acid) obtained in 1,4-dioxane was partially insoluble in all solvents (~40%).

The polymers having free carboxyl groups [poly(propiolic acid), poly(acetylenedicarboxylic acid), and poly(phenylpropiolic acid)] were infusible up to 300°C probably owing to strong hydrogen bonding. Poly(methyl propiolate) softened at 253°–256°C. Weight loss started as low as at 100°C in the thermogravimetrical analysis of poly(propiolic acid), whereas no weight loss was observed below 220°C for poly(methyl propiolate).

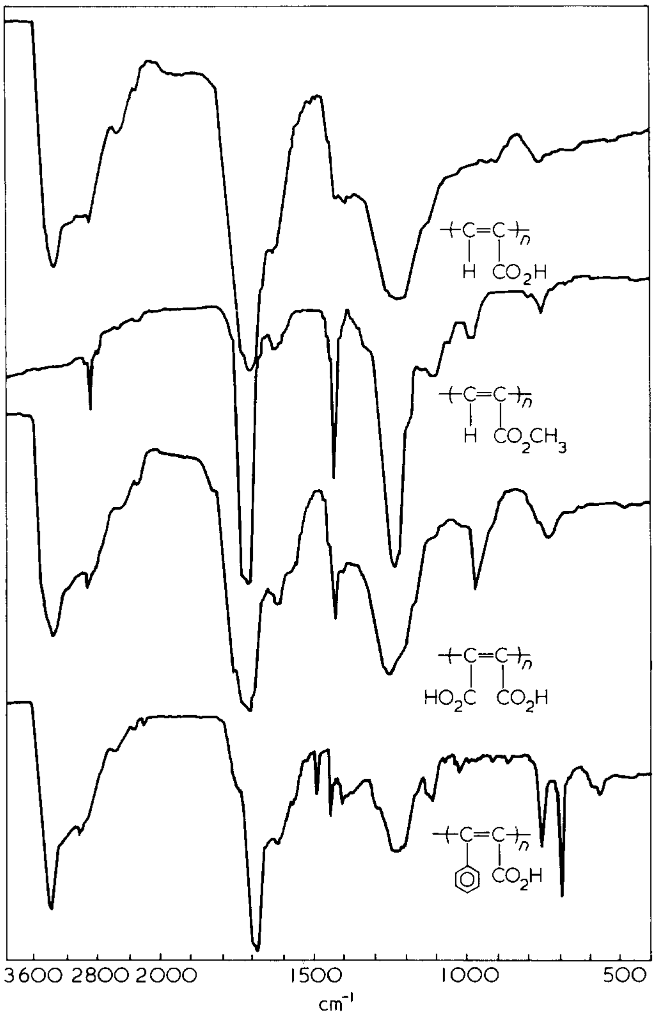

Figure 2 I.r. spectra of polymers from propiolic acid and its derivatives

Figure 2 shows the i.r. spectra of the polymers. Every corresponding monomer had an absorption at 2200–2100 cm^{-1} due to the $C \equiv C$ stretching, which is not observed in the spectra of polymers. The acid polymers show bands at 3500–2400 (OH), $\sim$1700 (C=O), $\sim$1620 (conjugated C=C), 1250–1200 cm^{-1} (C–O). Besides them, absorptions characteristic of phenyl group (760 and 690 cm^{-1}) are observed for poly(phenylpropiolic acid). However, poly(methyl propiolate) shows no band due to the OH stretching. In this way, these spectra qualitatively support the expected polymer structures shown in *Figure 2*.

The ^{13}C n.m.r. spectrum of poly(propiolic acid) in $(CD_3)_2SO$ consisted of the following signals: δ 166.8 ($-CO_2H$), 140.9 ($-CH=$), 129.2 [$C(CO_2H)-$]. This spectrum confirms the structure, $\mathrm{[CH=C(CO_2H)]}_n$.

REFERENCES

1 Khutareva, G. V., Krentsel, B. A., Shishkina, M. V. and Davidov, B. E. *Neftekhimiya* 1965, **5**, 90
2 Davidov, B. E., Krentsel, B. A. and Khutareva, G. V. *J. Polym. Sci. (C)* 1967, **16**, 1365
3 Masuda, T., Hasegawa, K. and Higashimura, T. *Macromolecules* 1974, **7**, 728
4 Masuda, T., Okano, Y., Kuwane, Y. and Higashimura, T. *Polym. J.* 1980, **12**, 907
5 Okano, Y., Masuda, T. and Higashimura, T. *Polym. J.* submitted
6 Masuda, T., Thieu, K.-Q., Sasaki, N. and Higashimura, T. *Macromolecules* 1976, **9**, 661
7 Sasaki, N., Masuda, T. and Higashimura, T. *Macromolecules* 1976, **9**, 664
8 Masuda, T., Kawai, H., Ohtori, T. and Higashimura, T. *Polym. J.* 1979, **11**, 813
9 Kern, R. J. *J. Polym. Sci. (A-1)* 1969, **7**, 621
10 Akopyan, L. A., Grigoryan, S. G., Yegurtdzhyan, Sh. T. and Matsoyan, S. G. *Vysokomol. Soedin (A)* 1975, **17**, 1072
11 Akopyan, L. A., Grigoryan, S. G., Zhamkochyan, G. A. and Matsoyan, S. G. *Vysokomol. Soedin. (A)* 1975, **17**, 2517