behavior of the copolymerization of HCX with St, the behavior of homopolymerization of QM,[3] and the paramagnetic character of the QM derivatives[3,6] that the propagation in those polymerizations may be very close to a radical coupling type and stepwise reaction between the polymer active site and the biradical of the QM derivatives. In the copolymerization of HCX with St, a polymer active site with the terminal unit of HCX is considered to react with St *via* the common mechanism of the radical addition to the carbon-carbon double bond and, then, the resulting polymer active site reacts with HCX *via* the radical coupling mechanism. If the copolymerization does not start in high St monomer feed, the former polymer active site reacts with HCX *via* the latter mechanism to yield the homopolymer of HCX or copolymers with the predominant HCX unit content. The latter polymer active site reacts exclusively with HCX because of the great difference in reactivity of both monomers. The latter step of radical coupling is considered to play an important role in this copolymerization.

References and Notes

(1) M. Szwarc, *Nature (London)*, **160**, 403 (1947).
(2) For instance, see L. A. Errede and M. Szwarc, *Quart. Rev., Chem. Soc.*, **12** 301 (1958); and Y. Minoura; "New Polymerizarion Reaction" (in Japanese) T. Saegusa, Ed., Kagaku Dojin Co., Kyoto, Japan, 1971 p 7.
(3) L. A. Errede, R. S. Gregorian, and J. M. Hoyt, *J. Amer. Chem. Soc.*, **82**, 5218 (1960).
(4) L. A. Errede and J. M. Hoyt, *J. Amer. Chem. Soc.*, **82**, 436 (1960).
(5) H. G. Gilch, *Angew. Chem.*, **77**, 592 (1965).
(6) H. G. Gilch, *J. Polym. Sci., Part A-1*, **4**, 438 (1966).
(7) M. Ballester, J. Castaner, and J. Riera, *J. Amer. Chem. Soc.*, **88**, 957 (1966).
(8) S. Iwatsuki and T. Kokubo, unpublished result.
(9) M. Ballester, C. Molinet, and J. Castaner, *J. Amer. Chem. Soc.*, **82**, 4254 (1960).
(10) The uv spectrum of TCX in cyclohexan:[5] 349 (ϵ 45,000), 331 (26,000), 316 (9200), and 247 nm (6300).
(11) S. Iwatsuki and H. Kamiya, unpublished results.
(12) F. R. Mayo and G. Goldfinger, *J. Amer. Chem. Soc.*, **66**, 1594 (1944).
(13) T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).
(14) F. T. Wall, *J. Amer. Chem. Soc.*, **66**, 2050 (1944).
(15) F. A. Bovey, G. V. D. Tiers, and G. Filipovich, *J. Polym. Sci.*, , 73 (1959).
(16) Principle of the treatment was based on the following papers: T. Kagiya, M. Hatta, and K. Fukui, *Kobunshi Kagaku*, **23**, 730, 737 (1963).

Organometallic Polymers. XXX. Synthesis and Copolymerization of η^6-(2-Phenylethyl methacrylate)tricarbonylchromium with Organic Monomers

C. U. Pittman, Jr.,*[1a] O. E. Ayers,[1a,b] and S. P. McManus[1c]

Department of Chemistry, University of Alabama, University, Alabama 35486, and the Department of Chemistry, University of Alabama in Huntsville, Huntsville, Alabama 35807.

Received October 11, 1973

ABSTRACT: The monomer η^6-(2-phenylethyl methacrylate)tricarbonylchromium (PEMATC) was synthesized and copolymerized in ethyl acetate solutions at 70° with acrylonitrile, methyl methacrylate, and styrene using azobisisobutyronitrile (AIBN) as the free-radical initiator. The reactivity ratios of each of the comonomer pairs were determined using the integral form of the copolymer equation on copolymerizations to higher yields. M_1 is defined as the organometallic monomer. The ratios were: PEMATC–styrene $r_1 = 0.04$, $r_2 = 1.35$; PEMATC–acrylonitrile $r_1 = 0.07$, $r_2 = 0.79$; PEMATC–methyl methacrylate $r_1 = 0.09$, $r_2 = 1.19$. A classic r_1, r_2 determination using low conversion polymerizations, at several different M_1^0/M_2^0 ratios, gave reactivity ratios very close to those stated above. Microgel formation and binodal gel permeation chromatograms were frequently observed in the high conversion runs, but such processes had little effect on the reactivity ratios since the low conversion runs were free of these complications. Q–e maps were prepared for the PEMATC copolymerizations, but no values of Q or e could be assigned to PEMATC which were consistant for all the copolymerizations. The copolymerization behavior of PEMATC was compared to the related monomers η^6-(2-phenylethyl acrylate)tricarbonylchromium and η^6-(benzyl acrylate)tricarbonylchromium. PEMATC readily homopolymerized in ethyl acetate at 70° to give homopolymers with $\bar{M}_n$ values of 15,000–20,000. Thermal decomposition of PEMATC polymers resulted in a slow destruction of the η^6-benzenetricarbonylchromium units, both in air and under nitrogen, with the formation of CO, insoluble polymers, and chromium oxides dispersed in the polymers.

The synthesis of polymers[2–4] containing organometallic monomers and investigations of their properties[2a,5,6] have recently accelerated in scope. The radical-initiated vinyl addition homopolymerization and copolymerization of a variety of organometallic monomers, such as η^6-styrenetricarbonylchromium,[7] vinylcyclopentadienylmanganese tricarbonyl,[2a,8] vinylferrocene,[9] η^6-(benzyl acrylate)tricarbonylchromium,[10] ferrocenylmethyl acrylate[11,12] and methacrylate,[11,12] and 2-ferrocenylethyl acrylate[13] and methacrylate[13] have now been well established.

Only a few organochromium monomers have been synthesized and polymerized. These include η^6-styrenetricarbonylchromium,[7] η^6-(benzyl acrylate)tricarbonylchromium,[10] and η^6-(2-phenylethyl acrylate)tricarbonylchromium.[14] η^6-(Benzyl acrylate)tricarbonylchromium has been homopolymerized and copolymerized with both styrene and methyl acrylate to give high molecular weight polymers.[10] η^6-Styrenetricarbonylchromium has been readily copolymerized with styrene ($r_1 = 0$, $r_2 = 1.39$) and methyl acrylate ($r_1 = 0$, $r_2 = 0.75$), but it would not homopolymerize.[7] η^6-(2-Phenylethyl acrylate)tricarbonylchromium has been copolymerized with styrene, methyl acrylate, acrylonitrile, and 2-phenylethyl acrylate using AIBN initiation.[14]

Polymers containing η^6-(aryl)tricarbonylchromium units are of interest because the thermal decomposition of this moiety within a polymer film might lead to the deposition of chromium metal or chromium oxides within that film in molecular sized units. Also these polymers could be of potential use as chromium catalysts.

Results and Discussion

η^6-(2-Phenylethyl methacrylate)tricarbonylchromium (hereafter PEMATC) was prepared by the route shown in eq 1. η^6-(2-Phenylethanol)tricarbonylchromium was syn-

Table I
Copolymerization of η^6-(2-Phenylethyl methacrylate)tricarbonylchromium (M_1) and Acrylonitrile (M_2) at 70° in Ethyl Acetate^a

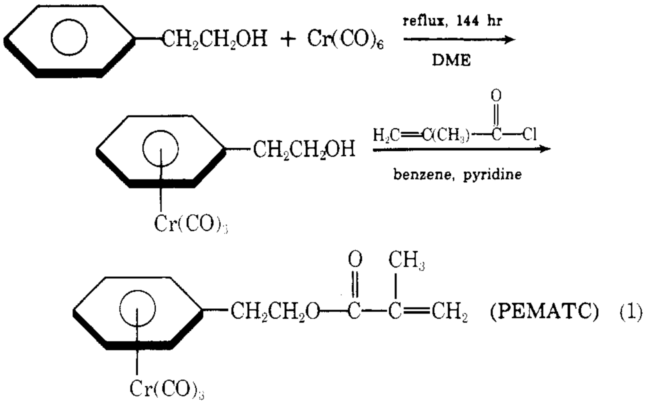
Polymer no.	Initial M_1, g	Initial mole ratio (M_1/M_2)	AIBN, g	Reaction time, hr	Yield, %	M_1 in copolymer, mol %
1	1.142	70/30	0.0122	1.0	5.6	45.6
2	1.142	70/30	0.0122	5.0	38.2	49.0
3	0.979	30/70	0.0135	1.0	7.1	27.2
4	0.979	30/70	0.0135	5.0	27.5	27.1
5	0.946	29/71	0.0132	1.0	8.9	25.8
6	0.946	29/71	0.0132	1.5	11.3	25.7
7	0.946	29/71	0.0132	2.0	15.0	26.0
8	0.946	29/71	0.0132	3.0	19.5	26.6
9	0.946	29/71	0.0132	3.0	20.1	26.3
10	1.591	97.5/2.5	0.0160	1.5	16.3	91.5
11	1.591	97.5/2.5	0.0160	1.5	16.1	86.2
12	1.591	97.5/2.5	0.0160	2.0	20.2	88.3
13	1.591	97.5/2.5	0.0160	1.5	17.1	88.3
14	1.591	97.5/2.5	0.0160	1.0	12.3	85.2

[a] 20 ml of ethyl acetate was used in each run.

Table II
Copolymerization of η^6-(2-Phenylethyl Methacrylate)tricarbonylchromium (M_1) and Methyl Methacrylate (M_2) at 70° in Ethyl Acetate^a

Polymer no.	Initial M_1, g	Initial mole ratio (M_1/M_2)	AIBN, g	Reaction time, hr	Yield,^{r} %	M_1 in copolymer, mol %
1	1.142	70/30	0.0129	2.0	21.2	41.7
2	1.142	70/30	0.0129	3.0	29.9	42.8
3	0.979	30/70	0.0168	2.0	22.6	20.6
4	0.979	30/70	0.0168	3.0	34.0	21.6
5	1.273	39/61	0.0188	1.0	18.5	27.6
6	1.273	39/61	0.0188	1.5	21.4	27.7
7	1.273	39/61	0.0188	1.5	21.1	28.2
8	1.273	39/61	0.0188	1.0	15.2	27.5
9	1.273	39/61	0.0188	1.5	20.1	27.9
10	1.591	97.5/2.5	0.0160	1.0	13.9	88.1
11	1.591	97.5/2.5	0.0160	1.5	16.3	87.5
12	1.591	97.5/2.5	0.0160	1.5	16.5	88.4
13	1.591	97.5/2.5	0.0160	2.0	20.5	88.1
14	1.591	97.5/2.5	0.0160	2.0	20.0	90.7

[a] 20 ml of ethyl acetate was used in each run.

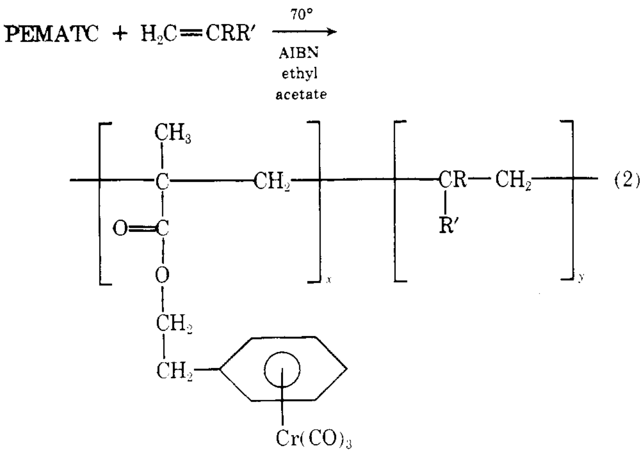


(1)

thesized from hexacarbonylchromium and 2-phenylethanol in refluxing 1,2-dimethoxyethane (DME) using a Strohmeier reactor. DME was an inert solvent and lowered the boiling point of the solution.

Attempts were made to synthesize PEMATC in anhydrous ethyl ether. However, repeated attempts to use ether as the solvent resulted in homopolymerization of PEMATC while the ether was being removed on a rotary evaporator at, or below, room temperature. Since the ethereal solution had been neutralized with bicarbonate, the polymerization did not result from residual acid. Apparently a small amount of peroxide, formed in the ether, initiated polymerization during work-up. Therefore, the esterification was run in dry benzene.

PEMATC was readily copolymerized with acrylonitrile, styrene, and methyl methacrylate as shown in eq 2. Copolymerizations were carried out at 70° in degassed ethyl ace-



(2)

R	R'
H	Ph
H	CN
CH_3	CO_2CH_3

Table III
Copolymerization of η^6-(2-Phenylethyl methacrylate)tricarbonylchromium (M_1) and Styrene (M_1) at 70° in Ethyl Acetate[a]

Polymer no.	Initial M_1, g	Initial mole ratio (M_1/M_2)	AIBN, g	Reaction time, hr	Yield, %	M_1 in copolymer, mol %
1	1.142	70/30	0.0130	2.0	6.6	41.9
2	1.142	70/30	0.0130	5.0	35.5	46.9
3	0.979	30/70	0.0171	2.0	13.1	20.4
4	0.979	30/70	0.0171	5.0	34.8	21.0
5	1.305	40/60	0.0193	1.0	8.8	25.8
6	1.305	40/60	0.0193	1.5	10.1	26.0
7	1.305	40/60	0.0193	3.0	20.2	26.2
8	1.305	40/60	0.0193	2.5	17.5	26.5
9	1.305	40/60	0.0193	3.0	19.1	26.1
10	1.591	97.5/2.5	0.0160	1.0	13.7	83.6
11	1.591	97.5/2.5	0.0160	1.5	16.6	86.8
12	1.591	97.5/2.5	0.0160	2.0	20.3	90.2
13	1.591	97.5/2.5	0.0160	2.0	18.5	89.3
14	1.591	97.5/2.5	0.0160	2.0	19.2	86.8

[a] 20 ml of ethyl acetate was used in each run.

Table IV
Reactivity Ratios for the Copolymerization of η^6-(2-Phenylethyl methacrylate)tricarbonylchromium (M_1) with Organic Monomers (M_2) at 70° in Ethyl Acetate Solutions

Monomer 2	r_1	r_2	Confidence limits[a] r_1 range	r_2 range
Acrylonitrile	0.073	0.794	0.039–0.137	0.657–0.958
Methyl methacrylate	0.089	1.19	0.067–0.119	1.09 –1.32
Styrene	0.041	1.35	0.015–0.108	1.20–1.52

[a] These are the extreme ranges of the approximate 95% joint confidence limits defined by the following equation from ref 16 where the values of t_1' and t_2' are solved for in: $(t_1' - \hat{t}_1)^2a_{11} + 2(t_1' - \hat{t}_1)(t_2' - \hat{t}_2)a_{12} + (t_2' - \hat{t}_2)^2a_{22} = 2s^2F\alpha(2,h)$.

tate solutions using AIBN as the initiator. Degassing of monomer solutions and work-up after polymerization were the same as previously reported in copolymerizations of organometallic monomers.[11,14] Results and experimental conditions for sample copolymerizations are summarized in Tables I–III. The polymerization time was usually designed to keep the conversion relatively low because calculations of r_1 and r_2 are best performed, even when using the integrated form of the copolymer equations, from runs to low conversions.[15] However, as a check on this method experiments were performed at very low conversions using classic m_1 vs. M_1^0 plots and fitting these data to the best values of r_1 and r_2. These will be discussed later.

Cross-linking, on exposure to light, occurred in the PEMATC copolymers on prolonged standing (several days in many cases) in solution and on long-term storage in the powder form. The ir spectra of the resulting cross-linked polymers were similar to those of the soluble polymers. Copolymers of η^6-(2-phenylethyl acrylate)tricarbonylchromium with styrene, methyl acrylate, acrylonitrile, and 2-phenylethyl acrylate, reported previously,[14] also have a tendency to undergo cross-linking upon standing in solution or in powder form.

Reactivity Ratios. The data in Tables I–III were used to calculate the reactivity ratios for these PEMATC copolymerizations. Initial copolymerizations were carried out at molar ratios (M_1^0/M_2^0) of 30/70 and 70/30. Crude estimates of r_1 and r_2 were obtained from these data using the Montgomery and Fry method.[15] Using these initial estimates of r_1 and r_2 and the computed tables prepared by Tidwell and Mortimer,[16] the following optimized initial mole ratios (M_1^0/M_2^0) were then selected for conducting further copolymerizations: PEMATC-AN, (M_1^0/M_2^0) = 29/71 and 97.5/2.5; PEMATC-MMA, (M_1^0/M_2^0) = 39/61 and 97.5/2.5; PEMATC-STY, (M_1^0/M_2^0) = 40/60 and 97.5/2.5. As shown in Tables I–III, copolymerizations were carried out to each of these new molar ratios and the data were then used to calculate "best" r_1 and r_2 values and also the approximate 95% joint confidence limits.[16] These reactivity ratios and joint confidence limits are reported in Table IV. They were calculated using the method advocated (and thoroughly discussed) by Tidwell and Mortimer.[16,17] Plots of the approximate 95% joint confidence limits are shown in Figure 1. As shown, the reactivity ratios were obtained with rather small confidence limits. Therefore, these ratios are considered to be far more reliable than the previous r_1 and r_2 values obtained for η^6-(2-phenylethyl acrylate)tricarbonylchromium.[14,18]

Using the reactivity ratios in Table IV, Q–e maps were prepared, but no common approximate values of Q or e could be assigned to PEMATC which were consistant for the three comonomers employed. The $-Cr(CO)_3$ moiety is known to be a strongly electron-withdrawing function[19,20] (as strong as a nitro group) in the absence of electron demand adjacent to the aryl ring and a strong electron donar in the presence of an electron demand.[20,21] However, it is difficult to see how this effect can become manifest during polymerization when the radical center is so far removed from the complexed ring and insulated from it by a carboethoxy group.

One possible explanation for the observed deviation from the Q–e scheme could involve a mechanism change as M_2 is varied from styrene to acrylonitrile. If progressive competition from a charge-transfer complex mechanism[22] occurred, as comonomers with larger positive values of e were used, the Q–e scheme would not apply (by definition). Little was known of the ability of the $Cr(CO)_3$ group to promote charge-transfer complexation of the aryl ring either by acrylonitrile or methyl acrylate. Thus ethyl acetate solutions of acrylonitrile and both benzenetricarbonylchromium and PEMATC were examined by uv. In the former a long wave-length charge-transfer band of low intensity was

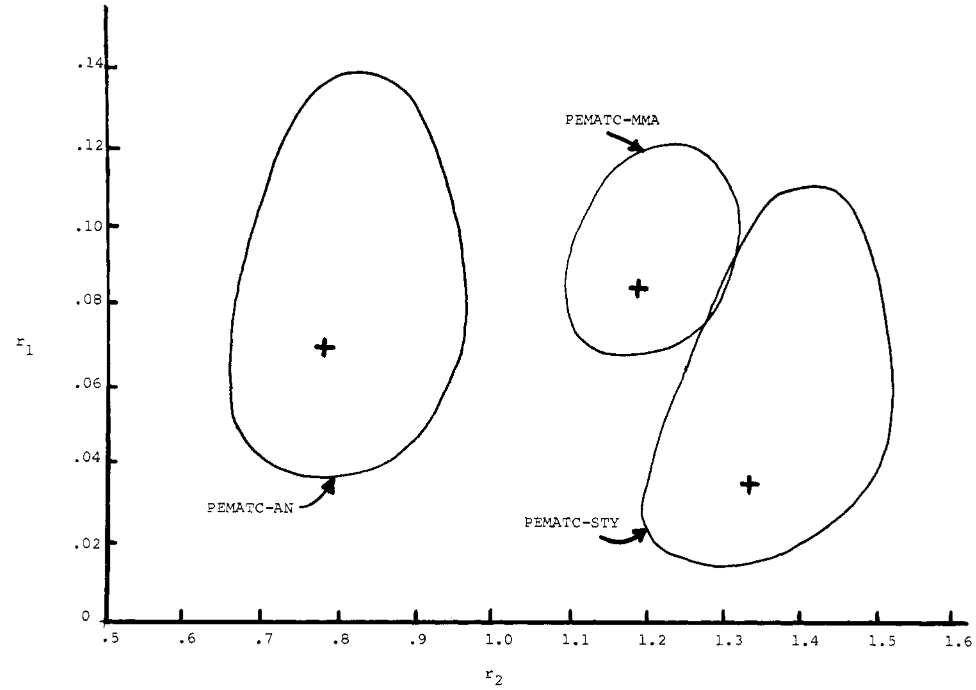


Figure 1. Approximate 95% joint confidence limits for the reactivity ratios of the copolymerizations of η^6-(2-phenylethyl methacrylate)tricarbonylchromium with acrylonitrile (AN), styrene (STY), and methyl methacrylate (MMA) derived from higher conversion data.

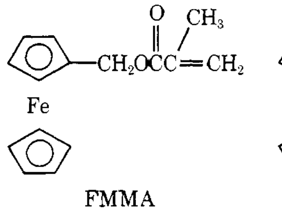
Table V
Comparison of the Reactivity Ratios of η^6-(2-Phenylethyl acrylate)tricarbonylchromium to Those of Related Organometallic Monomers with Common Organic Comonomers

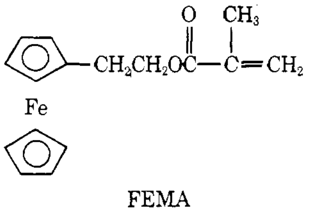
Comonomer (M_2)	Methyl methacrylate		PEMATC[a]		FMMA[a]		FEMA[a]	
	r_1	r_2	r_1	r_2	r_1	r_2[b]	r_1	r_2[c]
Styrene	0.46	0.52	0.04	1.35	0.03	3.7	0.08	0.58
Acrylonitrile	1.22	0.15	0.07	0.79	0.30	0.11		
Methyl methacrylate	1	1	0.09	1.19	0.12	3.27		
Methyl acrylate	1.5	0.3			0.08	0.82	0.20	0.65

[a] Abbreviations given for structures in the text. [b] Taken from ref 11 and 12. [c] Taken from ref 13.

observed at λ 695 nm while a similar λ 715 nm band was observed for PEMATC acetonitrile. These bands, not present when only the donar or the acceptor was present alone, *suggest* a charge-transfer complex is formed. However, the role such a species plays in the copolymerization process is, at best, speculative.

A common pattern arises when comparing the reactivity ratios for PEMATC vs. those of methyl methacrylate for a series of common comonomers. The r_1 values are lower and the r_2 values are greater for PEMATC copolymerizations *vs.* those of methyl methacrylate (see Table V). This is true over the entire range of e_2 values of the M_2 series used. In fact, this trend appears to be a general one for a series of related bulky organometallic monomers including ferrocenylmethyl methacrylate (FMMA) and ferrocenylethyl methacrylate (FEMA).[12,13]


FMMA


FEMA

This observation is most easily rationalized on steric grounds. The aryltricarbonylchromium and ferrocene moieties both have a large steric bulk. Unlike a planar benzene ring, these organometallic groups have a large depth (as well as length and width). Thus, when rotating, or when static, they require a greater volume. Electronic effects should not be a major factor (other than that portion of the copolymerization which may take place through charge-transfer complexes) because the organometallic function is well insulated from the vinyl group in every case. Already, it is well known[12,13] that FMMA exhibits smaller r_1 values with a variety of organic comonomers than does FEMA which, in turn, exhibits smaller r_1 values than methyl acrylate. Certainly, steric effects are operative in this series. A quantitative evaluation of steric effects is not yet possible.

Copolymer Characterization. Examples from each set of copolymers were characterized by infrared, gel permeation chromatography, intrinsic viscosity measurements, and differential scanning calorimetry. The monomer ratio in every copolymer was established by specific, duplicate (atomic absorption) chromium analysis. Copolymers produced in the low conversion studies were analyzed for Cr, C, H, and N (where acrylonitrile was M_2). The ir spectra are summarized in the Experimental Section for each type copolymer. All the copolymers were soluble in ethyl acetate, acetone, and tetrahydrofuran. Benzene is a poor solvent for copolymers with substantial mole fractions of PEMATC, and only lower molecular weight fractions dissolve.

Intrinsic viscosity measurements were carried out in THF at 30°. The copolymers were characteristic of gel permeation chromatography, and estimates of the molecular weights were then obtained by universal calibration.[23,24] Example intrinsic viscosity and molecular weight data are given in Table VI. Chromatograms were either binodal

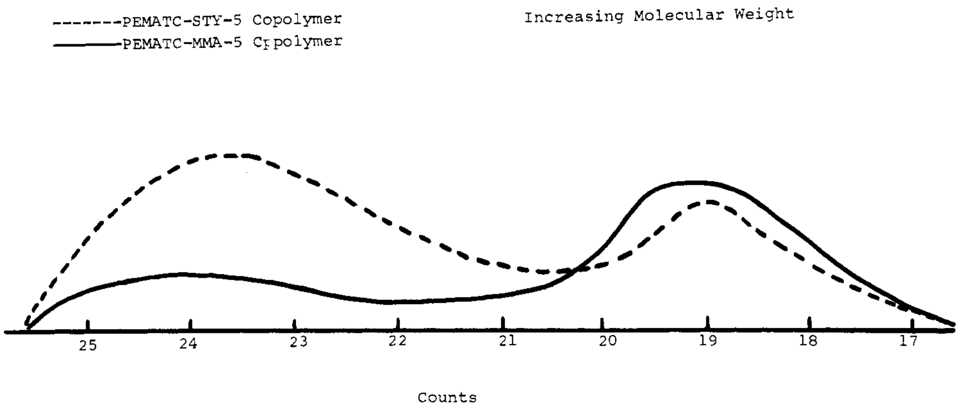


Figure 2. Gel permeation chromatograms of PEMATC-MMA and PEMATC-STY copolymers.

Table VI
Molecular Weight and Intrinsic Viscosity Determinations for a Representative Series of Copolymers of η^6-(2-Phenylethyl methacrylate)tricarbonylchromium (PEMATC)

Copolymer no.[a]	Mol % M_1 in copolymer	$[\eta]$, dl/g	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
PEMATC-AN-5	25.85	0.280	2,500	36,000	14.5
PEMATC-AN-10	91.51	0.127	7,500	166,000	22.0
PEMATC-MMA-2	42.79	0.062	16,400	8×10^6[b]	500
PEMATC-MMA-5	27.55	0.060	38,400	11×10^6[b]	290
PEMATC-STY-4	21.03	0.186	7,600	3.4×10^6[b]	460
PEMATC-STY-5	25.75	0.120	14,000	3.8×10^6[b]	270

[a] Copolymer numbers refer to those in Tables I–III and AN = acrylonitrile, MMA = methyl methacrylate, and STY = styrene. [b] High $\bar{M}_w$ values, along with high values of $\bar{M}_n/\bar{M}_w$, were obtained due to the binodal nature of the gpc chromatograms. Portions of the high molecular weight nodes appeared to exceed the column bank's resolution limits.

(two distinct peaks) or they exhibited a smooth peak with a tail or plateau. Figure 2 illustrates the gpc chromatograms for PEMATC-MMA and PEMATC-STY copolymers. The PEMATC-AN copolymers exhibited only monomodal chromatograms. Sample molecular weight values for the PEMATC copolymers are listed in Table VI. In the cases of copolymers of PEMATC with methyl methacrylate and styrene, very high $\bar{M}_w$ values were obtained and portions of the polymers exceeded the gpc column resolution limits. Copolymers of η^6-(2-phenylethyl acrylate)tricarbonylchromium with styrene, methyl acrylate, and 2-phenylethyl acrylate, prepared previously,[13] also gave binodal gpc chromatograms. In all cases the very high molecular weight copolymer fractions probably resulted from branching and at higher conversions microgel formation occurred.

PEMATC was homopolymerized in ethyl acetate using AIBN as the free radical initiator at 70°. In solutions containing 2.0 g of PEMATC per 20 ml of ethyl acetate, yields of 35% were obtained after 3 hr using 1% weight AIBN for initiation. A more concentrated solution consisting of 4.0 g of PEMATC in 20 ml of ethyl acetate gave a yield of 64.8% homopolymer after 3 hr. In this polymerization, 0.5% weight of AIBN was added initially and a like amount 1.5 hr later. Gellation occurred during the homopolymerization of PEMATC resulting in some polymer that was insoluble in ethyl acetate. Soluble PEMATC homopolymers exhibited $\bar{M}_n$ values between 15,000 and 20,000 but very high $\bar{M}_w$ values. Gel formation was pronounced in the PEMATC homopolymers after 3 hr of reaction time at 70°. Only the THF soluble fraction was used in the molecular weight determinations.

Reactivity Ratio Studies of Low Conversion Studies. The use of the copolymerization experiments in Tables I–III to give the reactivity ratios in Table IV is subject to a valid criticism. There is little direct evidence in that data that normal copolymerization occurred, and it was suggested by a reviewer that the phenyltricarbonylchromium group acts as a powerful chain transfer agent. Certainly microgel formation, molecular weight data (Table VI), binodal gpc, and solubility data tend to confirm this observation. *Thus, in order for the relative reactivity data (Table IV, Figure 1) to be meaningful, it had to be shown that chain transfer and branching was not causing fundamental changes in r_1 and r_2.* Therefore, for each comonomer pair a series of classic copolymerizations of PEMATC and M_2 were carried out at very low conversions over M_1^0/M_2^0 ratios of 96/4 to 5/95. The copolymers obtained under these conditions were mononodal and no gel was detected. Conversions were kept below 3.6% in every case and below 2.8% in most runs.

These data are summarized in the plots shown in Figures 3–5. The experimental points on these m_1 vs. M_1^0 graphs fall within the ranges expected based on the r_1, r_2 values in Table IV. These plots show the areas encompassed by curves generated from data in Table IV using the "best," the low–low, the high–high, the high–low, and the low–high r_1 and r_2 values from Table IV (derived from the higher conversion studies). On these graphs the experimental points of low conversion (<3%) runs are shown. *It can be seen at once that they fall within the joint confidence intervals predicted from the higher conversion studies. Therefore, branching or chain-transfer processes do not seem to seriously affect the rate of monomer incorporation in the copolymers within the limits of this study.*

Thermal Decomposition Studies. A PEMATC homopolymer and PEMATC–styrene copolymer number 6 (26.0 mol % PEMATC) were thermally decomposed in air and under nitrogen at 190–200°. The polymers turned from greenish-yellow to light green as the η^6-(aryl)-$Cr(CO)_3$ units disappeared during thermal decomposition. After decomposition, the polymers were only partially soluble in ethyl acetate and acetone because of cross-linking which occurred during the heating. After 3 hr of heating in the presence of air, the chromium carbonyl groups of the PEM-

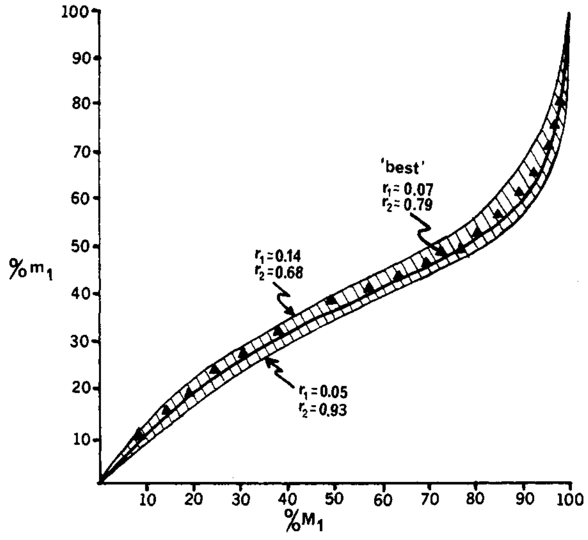


Figure 3. Low conversion composition-conversion plot of PEMATC (M_1) and acrylonitrile (M_2). Area encompasses that area given by the 95% confidence intervals of the r_1, r_2 data obtained at higher conversitions. Triangles (▲) represent low conversion experimental points obtained in ethyl acetate at 70°.

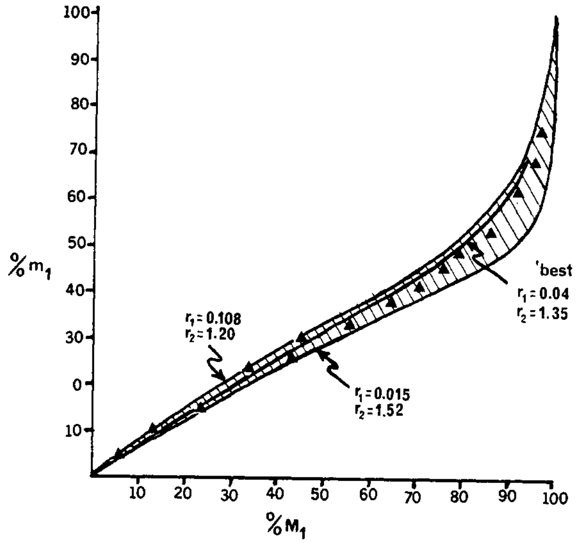
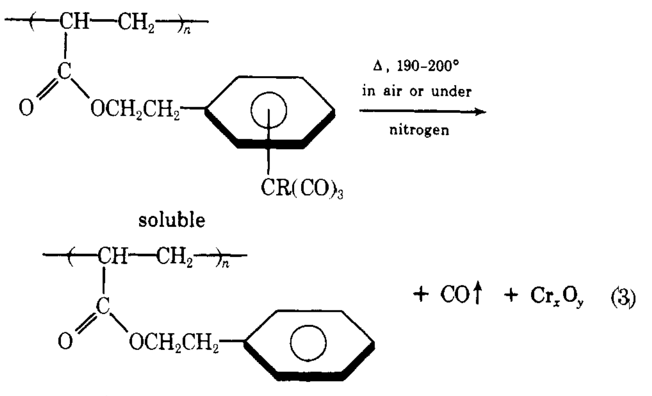


Figure 4. Low conversion composition-conversion plot of PEMATC (M_1) and styrene (M_2). Area shown encompasses that area given by the 95% joint confidence intervals of r_1 and r_2 data obtained at higher conversion. Triangles (▲) represent low conversion experimental points obtained in ethyl acetate at 70°.

ATC homopolymer and copolymer had completely disappeared as shown by infrared. However, when the two polymers were thermally decomposed under nitrogen for 3 hr, a significant number of the metal carbonyl groups remained intact. The metal carbonyl groups exhibit intense bands at 1960 and 1875 cm^{-1}. In both the homo- and copolymer, the intensities of the metal carbonyl bands decreased with elevated temperature and time. The chemical nature of the chromium (oxides) produced during these decomposition reactions is not known.

Samples of the PEMATC homopolymer and PEMATC–styrene-6 copolymer were thermally decomposed under vacuum and the gaseous product was analyzed for CO. After heating for 1.5 hr at 190–200°, mass spectrographic analysis of the gaseous product of the PEMATC homopolymer gave 76.5% CO and 1.5% CO_2, while the gaseous product from the copolymer contained 74.2% CO and 0.4% CO_2. Thus, the main gaseous product in the thermal decomposition of PEMATC polymers in an evacuated system is CO.



(3)

Experimental Section

Materials. Commercially available samples of reagent grade styrene, acrylonitrile, and methyl methacrylate were purified by vacuum distillation before use. PEMATC was prepared by the following procedure.

Synthesis of η^6-(2-Phenylethanol)tricarbonylchromium. η^6-(2-Phenylethanol)tricarbonylchromium was prepared by the direct reaction of hexacarbonylchromium with 2-phenylethanol in a Strohmeier[25] reactor. A large Strohmeier reactor was flushed with dry nitrogen and charged with hexacarbonylchromium (50 g, 0.277 mol), 2-phenylethanol (278 g, 2.29 mol), and 1,2-dimethoxyethane (150 g, 1.67 mol). The 2-phenylethanol was dried over anhydrous calcium chloride and vacuum distilled before use. Purification of 1,2-dimethoxyethane was accomplished by drying over sodium and then vacuum distilling before addition to the reactor. The 1,2-dimethoxyethane (DME) serves as an inert solvent and lowers the boiling point of 2-phenylethanol.

A temperature of 140–150° was maintained in the reaction pot for 144 hr or until there was no evidence of any white deposit of hexacarbonylchromium in the upper condenser portion of the Strohmeier apparatus. The greenish-yellow solution was allowed to cool and then transferred to a round-bottom flask (1000 ml). Unreacted 2-phenylethanol and DME were removed with a rotary evaporator at reduced pressure (100° (0.1 mm)) to give a viscous greenish-yellow oil. The viscous oil was dissolved in ethyl ether (500 ml) and filtered to remove the green colored insoluble chromium products. After removing the ether with a rotary evaporator, the remaining yellow viscous oil was recrystallized twice from a 75/25 v/v *n*-pentane–ethyl ether mixture. Upon filtering and drying in a vacuum oven (10^{-2} mm), a yield of 51.0 g (87.0%) of η^6-(2-phenylethanol)tricarbonylchromium was obtained as yellow needle-like crystals: mp 51–52° (lit.[14,16] mp 53–54°); ir (KBr) 3340 (OH s), 3100, 2960, 2890, 1950 (CO s), 1890–1850 (CO s), 1525, 1455, 1418, 1375, 1150, 1050, 1015, 995, 950, 812, 660, and 630 cm^{-1}; nmr (CCl_4) δ 1.79 (s, 1, OH), 2.61 (m, 2, $ArCH_2$), 3.86 (m, 2, CH_2O), 5.29 (br s, 5, aromatic hydrogens). *Anal.* Calcd for $C_{11}H_{10}O_4Cr$: C, 51.12; H, 3.88; Cr, 20.14. Found: C, 51.31; H, 3.95; Cr, 19.75.

Synthesis of η^6-(2-Phenylethyl methacrylate)tricarbonylchromium. η^6-(2-Phenylethanol)tricarbonylchromium (10.33 g, 0.04 mol) and dry pyridine (6.87 g, 0.086 mol) were added to a 1-l. flask containing dry, distilled benzene (400 ml) and equipped with a condenser, mechanical stirrer, and pressure equalizing addition funnel. The flask and attachments had been dried in a hot oven (110°) and purged with dry nitrogen before addition of the solvent and reactants. After cooling in an ice bath (0°), a solution of methacrylyl chloride (9.0 g, 0.086 mol) in dry benzene (40 ml) was added dropwise to the rapidly stirred solution over a 30-min period. Pyridine hydrochloride precipitated immediately upon the addition of the acid chloride. After this addition was completed, the solution was allowed to warm-up to room temperature and stirring continued for about 2 hr. The reaction product was diluted with additional benzene (200 ml) and filtered to remove the precipitated pyridine hydrochloride. Additional product was obtained by thoroughly washing the pyridine hydrochloride twice with benzene (150-ml portions) and combining the washings with the product solution. This benzene solution was then washed four times with saturated aqueous sodium bicarbonate solution (300-ml portions), three times with 10% sodium chloride solution (300-ml portions), and finally four times with distilled water (300-ml portions). These washings employed a mechanical stirrer to agitate the solutions to

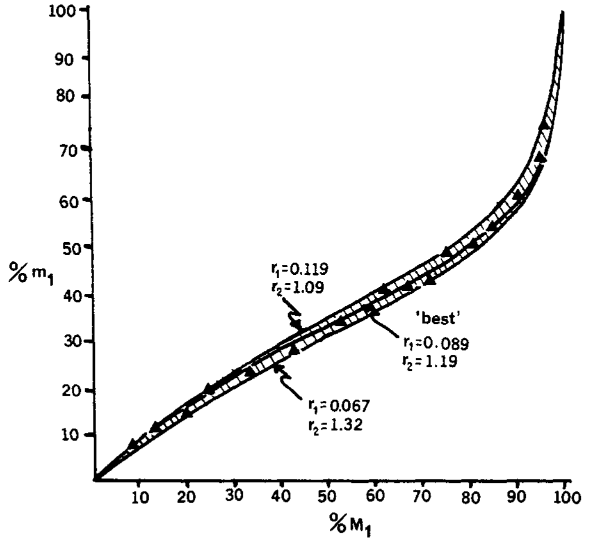


Figure 5. Low conversion composition–conversion plot of PEMATC (M_1) and methyl methacrylate (M_2) copolymerizations. Area in plots encompasses that area given by the 95% joint confidence intervals of the r_1 and r_2 data obtained at higher conversions. Triangles (▲) represent low conversion experimental points obtained in ethyl acetate at 70°.

effect neutralization and then use a separatory funnel to separate the organic phase from the aqueous phase. After drying over magnesium sulfate, the benzene solution was filtered and the solvent removed on a rotary evaporator (at room temperature in order to prevent possible homopolymerization of the monomer).

The crude product should be protected from light and air by keeping it dark and under a nitrogen atmosphere. Also during purification, the chromatographic column should be protected from the light and a nitrogen atmosphere used during separation of ester.

The resulting brownish-yellow viscous oil was purified by column chromatography on 70–325 mesh silica gel (30 g) using benzene as the elutant for the ester. After removing the benzene from the eluted product at room temperature, 7.5 g (57.6%) of viscous yellow η^6-(2-phenylethyl methacrylate)tricarbonylchromium was obtained. The product was crystallized from *n*-hexane at −20° to yield a yellow powder: mp 52–53°; ir (KBr) 3095, 3040, 2965, 2940, 1965 (CO s), 1900–1855 (CO s), 1715 (ester CO s), 1632, 1525, 1450, 1415, 1400, 1370, 1315, 1290, 1160, 1070, 1040, 1010, 990, 940, 810, 745, 698, 660, and 625 cm^{-1}; nmr ($CDCl_3$) δ 1.94 (s, 3, $CH_3C{=}C$), 2.55–2.83 (br m, 2, $ArCH_2$), 4.31 (m, 2, CH_2O), 5.17–5.67 (br m, 5, aromatic hydrogens), 5.94–6.22 (m, 2, $C{=}CH_2$). *Anal.* Calcd for $C_{15}H_{14}O_5Cr$: C, 55.21; H, 4.32; Cr, 15.94. Found: C, 55.42; H, 4.41; Cr, 15.65.

Copolymerizations. The copolymerizations were conducted in ethyl acetate, using the technique previously described.[11,26,27] All the polymerizations reported in this study were carried out at a temperature of 70°.

Copolymer Characterization. The universal calibration technique[23,24] used in these studies has been thoroughly described by Grube.[28] The copolymers resulting from the copolymerization of η^6-(2-phenylethyl methacrylate)tricarbonylchromium with styrene, acrylonitrile (AN), and methyl methacrylate (MMA) were characterized by infrared, differential scanning calorimetry, gel permeation chromatography (gpc), viscosity measurements, thermal decompositions, and elemental analysis. Monomer ratios in the copolymers were determined by chromium elemental analysis (by atomic absorption spectroscopy). Gel permeation chromatograms were run in tetrahydrofuran (THF) at 30° on a Waters Model 301 GPC. Viscosity measurements were made in dry distilled THF at 30° using a Cannon-Ubbelohde dilution viscometer. The intrinsic viscosities were estimated to range from a low of 0.06 dl/g for copolymer PEMATC-MMA-5 to a high of 0.28 dl/g for copolymer PEMATC-AN-5. Glass transition temperatures (T_g) of the copolymers were determined by dsc under an inert atmosphere of nitrogen. Infrared spectra were run on the purified copolymers in KBr pellets using a Perkin Elmer Model 521 spectrophotometer. Key ir bands are summarized below for one example of each copolymer system.

PEMATC–acrylonitrile copolymer: (KBr) 3080, 2980–2930, 2240 (CN s), 1955 (CO s), 1865 (CO s), 1795, 1715 (ester CO), 1520, 1445, 1380, 1285, 1215, 1150, 990, 805, 740, 690, 680, 655, 625, 525, and 465 cm^{-1}.

PEMATC–methyl methacrylate copolymer: (KBr) 3080, 2990, 2950, 2840, 1955 (CO s), 1870 (CO s), 1795, 1720 (ester CO s), 1445, 1380, 1310, 1285, 1240, 1145, 985, 805, 740, 690, 680, 655, 620, 525, and 465 cm^{-1}.

PEMATC–styrene copolymer: (KBr) 3065, 3030, 2980, 2935, 1960 (CO s), 1875 (CO s), 1795, 1715 (ester CO s), 1590, 1485, 1445, 1380, 1310, 1290, 1150, 1060, 990, 800, 750, 695, 655, 625, 530, and 470 cm^{-1}.

The experimental and characterization data for the copolymers of η^6-(2-phenylethyl methacrylate)tricarbonylchromium are summarized in Tables I–V.

Thermal Decomposition. Homopolymer PEMATC-1 (0.10 g) and copolymer PEMATC–styrene-6 (0.10 g) were placed in separate glass test tubes and heated in an oil bath for 3 hr at 190–200° exposed to the air. The polymers underwent a change in color from greenish-yellow to light green. Infrared spectra were run to monitor the decomposition before, during, and after heating. The thermally decomposed polymers were insoluble in acetone, ethyl acetate, THF, and benzene.

Small samples (0.10 g) of the two polymers listed above were thermally decomposed in tubes under an inert atmosphere (20 psi) of nitrogen. The samples were heated in sealed tubes under nitrogen for 3 hr at 190–200°. After heating, infrared spectra were run on the two polymers.

Also samples (0.10 g) of the two polymers were placed in Fisher-Porter tubes and evacuated (10−2 mm). The tubes were then placed in a heating oil bath and heated for 1.5 hr at 190-200°. After cooling to room temperature, the gaseous products were analyzed by mass spectrometry.

Acknowledgent. This research was supported in part by grants to Charles U. Pittman, Jr., from the Office of Naval Research and from the National Science Foundation, Grant No. GH-3766.

References and Notes

(1) (a) University of Alabama; (b) this work was taken from the Ph.D. Thesis of O. E. Ayers, University of Alabama, University, Alabama, 1973; (c) University of Alabama in Huntsville.

(2) (a) C. U. Pittman, Jr., B. V. Marlin, and R. D. Rounsefell, *Macromolecules*, **6,** 1 (1973); (b) C. U. Pittman, Jr., *Chem. Technol.*, **1,** 417 (1971).

(3) C. U. Pittman, Jr., *J. Paint Technol.*, **43,** 561 (1971); *Chem. Eng. News*, **48,** 36 (1970).

(4) E. W. Neuse and H. Rosenberg, *J. Macromol. Sci., Rev. Macromol. Chem.*, **4,** 1 (1970).

(5) D. O. Cowan, J. Park, C. U. Pittman, Jr., Y. Sasaki, R. K. Mukherjee, and N. A. Diamond, *J. Amer. Chem. Soc.*, **94,** 5110 (1972).

(6) N. Bilow, A. L. Landis, and H. Rosenberg, *J. Polym. Sci., Part A-1*, **7,** 2719 (1969).

(7) C. U. Pittman, Jr., P. L. Grube, O. E. Ayers, S. P. McManus, M. D. Rausch, and G. A. Moser, *J. Polym. Sci., Part A-1*, **10,** 379 (1972).

(8) C. U. Pittman, Jr., and P. L. Grube, *J. Polym. Sci., Part A-1*, **9,** 3175 (1971).

(9) J. C. Lai, R. D. Rounsefell, and C. U. Pittman, Jr., *J. Polym. Sci., Part A-1*, **9,** 651 (1971).

(10) C. U. Pittman, Jr., R. L. Voges, and J. Elder, *Macromolecules*, **4,** 302 (1971).

(11) J. C. Lai, T. D. Rounsefell, and C. U. Pittman, Jr., *Macromolecules*, **4,** 155 (1971).

(12) O. E. Ayers, S. P. McManus, and C. U. Pittman, Jr., *J. Polym. Sci.*, **11,** 1201 (1973).

(13) C. U. Pittman, Jr., R. L. Voges, and W. R. Jones, *Macromolecules*, **4,** 291, 298 (1971).

(14) C. U. Pittman, Jr., and G. V. Marlin, *J. Polym. Sci., Part A-1*, **11,** 2753 (1973).

(15) D. R. Montgomery and C. E. Fry, *J. Polym. Sci., Part C*, **25,** 59 (1968).

(16) P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci., Part A-1*, **3,** 369 (1965).

(17) P. W. Tidwell and G. A. Mortimer, *J. Macromol. Sci., Rev. Macromol. Chem.*, **4,** 281 (1970).

(18) G. V. Marlin, M.S. Thesis, University of Alabama, 1973.

(19) M. C. Whiting and B. Nicholls, *Proc. Chem. Soc., London*, 152 (1958); *J. Chem. Soc.*, 551 (1959).

(20) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, **4,** 324 (1965).

(21) D. K. Wells and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92,** 7461 (1970).

(22) J. A. Seiner and M. Litt, *Macromolecules*, **3,** 308, 312, 314, 316 (1971).

(23) Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., Part B*, **5,** 753 (1967).

(24) H. Coll and D. K. Gliding, *J. Polym. Sci., Part A-2*, **8**, 89 (1970).
(25) W. Strohmeier, *Chem. Ber.*, **94**, 2490 (1961).
(26) R. L. Voges, M.S. Thesis, University of Alabama, 1970.
(27) C. U. Pittman, Jr., R. L. Voges, and W. R. Jones, *Macromolecules*, **4**, 298 (1971).
(28) P. L. Grube, M.S. Thesis, University of Alabama, 1972.

The Polymerization of 2,4-Hexadiene. Stereoregular Polymer and the Mechanistic Study for Its Preparation

Mikiharu Kamachi,* Nobuhisa Wakabayashi, and Shunsuke Murahashi

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

Received March 13, 1974

ABSTRACT: The polymerization of 2,4-hexadienes has been carried out by various catalysts. High polymers were obtained from all isomers either by Lewis acids or transition-metal catalysts. Some transition-metal catalysts gave the stereoregular polymer composed of the erythrodiiso trans-1,4-tactic sequence. The study showed that the properties of transition metal and the isomeric form of monomer are important factors for the determination of configuration of the polymer. The crystalline polymer was prepared only with the trans,trans isomer by cobalt and titanium catalysts. The ligands in the catalyst and the polymerization solvent have little effect on the stereoregulation. *trans,trans*-2,4-Hexadiene was much more reactive than the corresponding trans,cis and cis,cis isomers by the transition-metal catalyst. This is in contrast to the result in the cationic polymerization. On the basis of these experimental results, the mechanism of the diene polymerization by transition-metal catalysis was discussed.

Extensive work has been reported on the polymerization of diene compounds, especially butadiene and isoprene, by transition-metal catalysts and their mechanisms.[1-5] We reported in a preliminary note[6] that 2,4-hexadiene could be polymerized to high polymers by using transition-metal catalysts or Lewis acids and that a crystalline polymer (erythrodiiso *trans-1,4-tactic*) was obtained using some of the former catalysts which gave the 1,4-cis polymer from butadiene[1,2,7] and the 1,4-cis or 1,2-trans polymer from 1,3-pentadiene.[8-10] The remarkable difference in the microstructure of the polymers obtained from similar diene compounds prompted us to an extensive investigation for the chemical structure of the crystalline polymer obtained from 2,4-hexadiene, the optimum condition for the preparation of the crystalline polymer, and then the mechanism of the polymerization by transition-metal catalysts.

To elucidate the difference in stereocontrol in the polymerization of diene compounds, several mechanisms have been proposed from the point of the coordination of the monomer or the structure of the propagating active end.[11-18] Recently, much information has been derived on the structure of the terminal active unit by the nmr technique.[19,20] Nevertheless, the mechanism of stereoregular polymerization of diene compounds by transition-metal catalysts still remains unsolved. It would be desirable for clarification of the polymerization mechanism to examine the polymerization of 2,4-hexadiene, which has three isomeric forms, by transition-metal catalysts.

In this communication, the detailed results of the polymerization of isomeric forms of 2,4-hexadiene are described. The microstructure of the polymer will be determined by various spectroscopy and then the condition for the preparation of stereoregular polymer will be examined. In addition, the mechanism of the stereoregular polymerization will be discussed on the basis of the above-mentioned results.

Experimental Section

(A) Monomers. The mixture of trans,trans and trans,cis isomers of 2,4-hexadiene were synthesized by the reaction of crotonaldehyde and ethylmagnesium bromide, followed by hydrolysis and subsequent dehydration of the alcohol (bp 80–81°, yield 51%). The isomer ratio of the mixture was determined by gas chromatography (column: silicon DC 550 on celite 545, 4.5 m) with helium as a carrier gas at 80°. The isomer ratio was trans,trans:cis,trans = 1:0.7. The cis,cis isomer could not be produced by this method. The cis,cis isomer was prepared by the isomerization of 1-*cis*-4-hexadiene (supplied from Toray Co. Ltd.) with Fe(acac)$_3$–Et$_3$Al as catalyst.[21] The isomer ratio of the product was trans,trans:trans,cis:cis,cis = 1:6:3.

The isomers were separated from their mixture by fractional distillation through a spinning band column. It was found by gas chromatography that each of the isomers thus separated had an isomeric purity of greater than 90%. These isomers were dried over calcium hydride before use in the polymerization.

(B) Solvents. Benzene and *n*-hexane were purified by ordinary methods and dried in a flask coated with sodium mirror.

(C) Catalysts. Commercial samples of boron trifluoride etherate, titanium tetrachloride, and organoaluminum compounds ($(C_2H_5)_2AlCl$ and $(C_2H_5)_3Al$) were purified by distillation under reduced pressure and stored under nitrogen at 0° as *n*-hexane solutions. Transition-metal acetylacetonates (M(acac)$_n$) were recrystallized from their benzene–hexane solutions and dried in high vacuum. M(acac)$_n$–Al(C_2H_5)$_2$Cl catalysts were prepared by adding *n*-hexane solution of Al(C_2H_5)$_2$Cl to mixtures of M(acac)$_n$ in benzene or *n*-hexane and shaking the solution for 30 min at 30°. The ratio of Al/Co was from 5 to 100. Commercial cobaltus halides (Cl, Br, and I) were purified by recrystallization from methanol solutions. Cobaltus halide pyridine complexes (CoX_2–2Py) were prepared by reacting CoX_2 (1 mol) with pyridine (2 mol) in ethyl alcohol and recrystallized from their ethanol solutions.

Transition-metal catalysts were prepared by introducing the reagents into a polymerization apparatus in the following order: polymerization solvents, transition metal compounds, and then aluminum compounds.

(D) Polymerization. The polymerizations by transition-metal catalysts were carried out in glass cylindrical tubes, having a side arm which was connected with a vacuum–nitrogen apparatus in order to remove the air from the reactor and to introduce nitrogen. The polymerizations were terminated by adding a small amount of methanol. The reaction mixture was then poured into a large amount of methanol containing aqueous HCl. The precipitated polymers were thoroughly washed with methanol and dried under vacuum at room temperature. They were usually purified by dissolving them in benzene and washing the solution with aqueous HCl in order to remove all inorganic moieties and then they were reprecipitated with methanol and dried under vacuum. The procedure for the cationic polymerization has been described elsewhere.[22] High-vacuum techniques were used for the anionic polymerization and radical polymerization. These methods have been shown in another communication.[23]

(E) Physical Examination of the Polymer. Intrinsic viscosities were determined in toluene at 30°, using a Ubbelohdetype viscometer. A nmr examination was performed with a Varian XL 100 spectrometer and a JEOL JNM-4H-100 spectrometer using solu-