Investigation of Kinetics of 4-Methylpentene-1 Polymerization Using Ziegler–Natta-Type Catalysts

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ABSTRACT: The kinetics of 4-methylpentene-1 (4MP1) polymerization by use of Ziegler–Natta-type catalyst systems, $M(acac)_3$-$AlEt_3$ (M = Cr, Mn, Fe, and Co), are investigated in benzene medium at 40°C. The effect of various parameters such as Al/M ratio, reaction time, aging time, temperature, catalyst, and monomer concentrations on the rate of polymerization and yield are examined. The rate of polymerization increased linearly with increasing monomer concentration with first-order dependence, whereas the rate of polymerization with respect to catalyst concentration is found to be 0.5. For all cases, the polymer yield is maximum at an Al/M ratio of 2. The activation energies obtained from linear Arrhenius plots are in the range of 25.27–33.51 kJ mol^{-1}. It is found that the aging time to give maximum percentage yield of the polymer varies with the catalyst systems. Based on the experimental results, a plausible mechanism is proposed that envisages a free-radical mechanism. Characterization of the resulting polymer product, for all the cases, through FTIR, ^{1}H-NMR, and ^{13}C-NMR studies, showed isomerized polymeric structures with 1,4-structure as dominant. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2468–2477, 2003

Key words: kinetics; isomer/isomerization; Ziegler–Natta; catalysts; polymerization

INTRODUCTION

Since the discovery of Ziegler–Natta catalysts, olefin polymerization and kinetics have been the subject of extensive research. Numerous works on the polymerization kinetics of α-olefins using such catalysts have been reported.[1,2] For higher α-olefins, the catalyst systems mostly examined for these studies are of heterogeneous type, consisting of titanium compounds such as the catalyst and $AlEt_3$ or $AlEt_2X$ (X = halide) as the cocatalyst. Thus, the polymerization kinetics of 1-butene and 1-pentene were studied with the $TiCl_3$-$AlEt_3$ catalyst system[3]; the polymerization kinetics of 1-hexene was studied with $TiCl_3$-$AlEt_2Cl$[4] and $TiCl_4$-$AlEt_3$[5] catalyst systems, and the polymerization kinetics of 1-octene was studied with $TiCl_4$-$AlEt_3$/$AlEt_2Br$,[6a] as well as with $MgCl_2$-supported $TiCl_4$-$AlEt_3$ catalyst systems.[6b]

Branched α-olefins were also studied with similar types of catalyst systems such as the polymerization kinetics of 3-methylbutene-1 with $TiCl_3$-$AlEt_3$,[7] of 1-phenylbutene-1 and 4-phenylbutene-1 with $TiCl_3$-$AlEt_3$,[8] the polymerization kinetics of 3-methylpentene-1 with $TiCl_3$-$AlEt_2Cl$,[9] and the polymerization kinetics of 4-methylpentene-1 with $TiCl_3$-$AlEt_3$[3,7] and also with the vanadium containing heterogeneous catalyst system VCl_3-AlR_3.[10]

Both the higher and the branched α-olefins were found to undergo monomer isomerization to the respective internal olefins during the polymerization[3,8,11] as well as during the copolymerization[12] with other monomers by using heterogeneous catalyst systems. The monomer isomerization in competition with polymerization is a significant problem in a large-scale polymer production, especially with branched α-olefins, where the proportion of the isomers in polymerized product is higher due to various possibilities of internal rearrangement of the substituent with respect to the olefinic bond and vice versa.

Despite the considerable amount of mechanistic details available for the polymerization kinetics of higher and branched α-olefins with heterogeneous catalyst systems, less is known with soluble, homogenous catalyst systems, specifically when the halogen atoms in the transition metal salts are replaced with organic groups or complex organic ligands.[3,13]

Thus, to shed some light on the efficiency of soluble, homogenous Ziegler–Natta-type catalytic systems and also to observe for the monomer isomerization polymerization with the selected catalyst system, we carried out in the present work a systematic kinetic study on the polymerization of 4-methylpentene-1 (4MP1), a liquid monomer which is thermodynamically the most unstable propylene dimer of the methyl pentenes, in benzene medium by using acetyl aceto-

TABLE I
Effect of the Reaction Time on the Rate of Polymerization, Molecular Weight of the Polymer, and Percentage Polymerization[a]

Reaction time, t (min)	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]				Molecular weight $\times 10^{-2}$				Percentage polymerization			
	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co
60	6.87	7.91	5.14	4.28	71	79	73	75	2.48	2.14	1.39	1.16
120	4.43	5.07	4.65	4.03	73	83	77	80	3.20	2.52	2.52	2.18
180	3.36	3.99	4.05	3.84	78	88	79	86	3.64	3.24	3.29	3.12
240	2.60	3.14	3.43	3.67	80	92	82	88	3.76	3.40	3.71	3.97
300	2.17	2.74	2.96	3.39	85	94	90	92	3.93	3.70	4.01	4.58

[a] Conditions: [4MP1] = 2 mol L^{-1}, [M(acac)$_3$] = 0.01 mol L^{-1}, [AlEt$_3$] = 0.02 mol L^{-1}, Al/M = 2, aging time = 15 min, temperature = 40°C.
[b] R_p = (1000 × w)/($M \times t \times v$), where w = weight of the polymer obtained after specified reaction time, M = molecular weight of the monomer, v = volume of the reaction mixture, and t = time of polymerization.

nates of various transition metals (viz., Cr, Mn, Fe, and Co) with triethyl aluminum as cocatalyst.

EXPERIMENTAL

Materials

The solvents benzene and methanol were purified according to standard procedures[14] and benzene was stored over sodium wire. The catalysts Cr(acac)$_3$,[15] Mn(acac)$_3$,[16] Fe(acac)$_3$,[17] and Co(acac)$_3$[18] were prepared according to the reported procedures. The cocatalyst triethyl aluminum was prepared by an already established procedure[19] and the purity was determined by estimating the amount of aluminum by EDTA titration, after hydrolyzing known quantities of the triethyl aluminum with dilute hydrochloric acid. The monomer 4MP1 (Fluka, USA) was distilled at 1 atm pressure and stored over clean sodium wire.

Polymerization

Polymerization reactions were carried out in a specially designed 50-mL Erlenmeyer flask with a B-19 cone joint fitted with a B-19 ground joint. Reagents were transferred by using an all-glass hypodermic syringe fitted with a stainless steel needle. Transfer of reagents to the flask was done inside a glove box,

which was continuously flushed with oxygen-free, ultrapure nitrogen. The required quantity of benzene was placed in the flask and a solution of the selected catalyst in benzene was added, followed by triethyl aluminum. The catalyst was allowed to age for specific time periods and then the required monomer was added. The flask was kept in a thermostat for reaction at a predetermined temperature. After the specified reaction time, the reaction was quenched by adding methanol containing 5% hydrochloric acid. The contents of the flask were then poured into a large excess of acidified methanol and left overnight when the polymer settled down. The polymer was washed with methanol, dried in vacuum oven at 40°C for 48 h, and weighed.

Polymer characterization

The intrinsic viscosities of all the polymers were determined in decalin at 130°C by using a Ubbelohde viscometer immersed in a silicone oil bath thermostat. The molecular weights of the polymers were calculated by using the following relationship derived by Hoffman et al.[20]:

$$[\eta] = 1.94 \times 10^{-4}(M_n)^{0.81}$$

TABLE II
Effect of Aging Time on the Rate of Polymerization, Molecular Weight of the Polymer, and Percentage Polymerization[a]

Aging time, t (min)	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]				Molecular weight $\times 10^{-2}$				Percentage polymerization[c]			
	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co
5	2.09	2.59	2.97	3.07	69	74	71	74	3.02	2.92	3.21	3.32
10	2.40	2.96	3.25	3.23	72	78	74	77	3.46	3.20	3.52	3.50
15	2.69	3.14	3.59	2.86	75	81	79	81	3.89	3.44	3.89	3.09
20	2.22	3.33	2.94	2.03	76	87	81	88	3.21	3.60	3.18	2.21
25	2.00	2.92	2.55	1.57	80	92	88	91	2.89	3.14	2.76	1.71

[a] Conditions: reaction time = 4 h, other conditions as in Table I.
[b] R_p is determined as in Table I.
[c] Percentage polymerization = [(weight of the polymer obtained)/(weight of the monomer in each run)] × 100.

TABLE III
Effect of Al/*M* Molar Ratio on the Rate of Polymerization, Molecular Weight
of the Polymer, and Percentage Polymerization[a]

Al/*M* molar ratio	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]				Molecular weight $\times 10^{-2}$				Percentage polymerization[c]			
	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co
1.0	2.21	2.91	2.64	2.73	61	63	66	59	3.19	3.14	2.86	2.95
1.5	2.71	3.46	3.20	3.31	73	87	78	78	3.91	3.74	3.46	3.58
2.0	3.41	3.94	3.61	3.79	82	89	84	84	4.92	4.26	3.91	4.10
2.5	2.81	2.12	2.71	3.39	71	76	62	73	3.92	2.29	2.93	3.67
3.0	2.60	1.04	1.18	2.91	64	59	59	69	3.35	1.13	1.28	3.15

[a] Conditions: reaction time = 4 h, other conditions as in Table I.
[b] R_p is determined as in Table I.
[c] Percentage polymerization as in Table II.

The polymers were characterized by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques. The IR spectra were recorded by using a Perkin–Elmer 598 spectrometer by incorporating the pure dry samples into dry KBr pellets. The ^{1}H-NMR spectra of the polymers were recorded on a Bruker 300 MHz spectrometer at 25°C in CDCl$_3$ solvent by using tetramethylsilane (TMS) as the internal standard. The ^{13}C-NMR spectra of the polymers were run at 25°C on a JEOL 400 MHz spectrometer operating at 100 MHz by using CDCl$_3$ as the solvent with TMS being the internal standard. The number of scans were in the range of 1000–3000. The ^{1}H-decoupling distortionless enhancement by polarization transfer (DEPT) technique was also employed to discriminate among carbon species by using the Bruker 300 MHz spectrometer at θ = 45°, 90°, and 135°. The quantitative evaluation of the structural units of the polymers was made by identifying the signals characteristic of various isomeric units and by the cutting–weighing method of the relevant peak areas. The molecular weight distribution analysis of the polymers was carried out with a Waters 150-CV GPC instrument with polystyrene as the internal standard. The M_w/M_n ratio of the resulting polymer varied between 2 and 3.

RESULTS AND DISCUSSION

Effect of reaction time

The reaction time for the polymerization of 4MP1 varied from 1 to 5 h. In all cases, rate increased rapidly, reaching a maximum value at 1 h, after which it decreased slowly. The molecular weights of the polymers with all the catalyst systems studied increased with time (Table I), similar to high-activity catalyst systems. This effect is characteristic of homogeneous[21–23] catalyst systems, which has been attributed to the decrease in the concentration of active centers present in the catalyst systems.[13,24]

Effect of aging time

The behavior of a catalyst system depends to a large extent on the order in which the catalyst components are mixed and on the presence of the monomer during the catalyst formation.[25] In the present work, triethyl aluminum solution was mixed with the transition–metal catalyst solution and allowed to age in the absence of the monomer. After the specified time, the monomer was added. The effect of the aging time was studied by varying it from 5 to 25 min. On adding triethyl aluminum solution, a dark-brown precipitate

TABLE IV
Effect of Catalyst Concentration on the Rate of Polymerization, Molecular Weight
of the Polymer, and Percentage Polymerization[a]

[*M*(acac)$_3$] $\times 10^2$ (mol L^{-1})	[*M*(acac)$_3$]$^{0.5}$ (mol L^{-1})	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]		Molecular weight $\times 10^{-2}$		Percentage polymerization[c]	
		Cr	Mn	Cr	Mn	Cr	Mn
0.9375	0.0968	1.91	2.24	72	71	2.75	2.42
1.2500	0.1118	2.56	3.12	78	84	3.69	3.37
1.8750	0.1369	2.84	3.69	86	89	4.09	3.99
2.8125	0.1677	3.38	4.42	83	82	4.88	4.78
3.75	0.1936	3.97	4.98	71	79	5.73	5.39

[a] Conditions: reaction time = 4 h, other conditions as in Table I.
[b] R_p is determined as in Table I.
[c] Percentage polymerization as in Table II.

TABLE V
Effect of Catalyst Concentration on the Rate of Polymerization, Molecular Weight
of the Polymer, and Percentage Polymerization[a]

$[M(acac)_3]$ (mol L^{-1})	$[M(acac)_3]^{0.5}$ (mol L^{-1})	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]		Molecular weight $\times 10^{-2}$		Percentage polymerization[c]	
		Fe	Co	Fe	Co	Fe	Co
0.015	1.225	2.41	2.50	73	79	2.61	2.71
0.025	0.1581	3.82	3.84	83	84	4.13	4.15
0.050	0.2236	4.48	4.60	86	86	4.85	4.98
0.075	0.2739	5.66	5.62	84	78	6.12	6.08
0.100	0.3162	6.32	6.43	79	71	6.84	6.96

[a] Conditions: reaction time = 4 h, other conditions as in Table I.
[b] R_p is determined as in Table I.
[c] Percentage polymerization as in Table II.

was formed with $Cr(acac)_3$ catalyst, the buff color of $Mn(acac)_3$ solution deepened, the rose colored $Fe(acac)_3$ solution turned dark red, and the green-colored $Co(acac)_3$ solution turned dark brown in the benzene medium irrespective of the concentration of catalyst. For all the catalyst systems, colors remained unchanged during the course of the polymerization, which indicates no complex formation with the monomer. The percentage yield of poly(4MP1) reached a maximum with aging time up to 15 min for Cr and Fe, 20 min for Mn, and 10 min for Co, and then decreased for all cases. The molecular weight of the polymers increased with the aging time (Table II).

Effect of Al/M ratio

It has been shown by many workers that the activity of the catalyst depends on the ratio between the catalyst and the cocatalyst. In the present study, the percentage polymerization of 4MP1 increased initially with increasing cocatalyst/catalyst ratio, reached a maximum, and then decreased. With all the catalyst systems under study, maximum conversion was observed at a ratio of 2. The molecular weights also showed a maximum at the optimum cocatalyst-to-catalyst ratio, resulting in the maximum conversion (Table III). These observations indicate the formation of active catalyst sites at this ratio. The ratio exhibiting maximum activity in the present study is in agreement

with the postulations of the formation of stoichiometric homogeneous complexes in solution.[21,26] The decrease in the molecular weights of polymers at a higher molar ratio indicates that the triethyl aluminum acts as a chain transfer reagent with the complex formed.[25a] The kinetic dependence of the polymerization rate on the triethyl aluminum concentration has been derived to be in the range of 0.5–1.0, which is explained by the shifting of the equilibrium to the right in the deduced mechanism.

Effect of catalyst concentration

The results of the effect of the variation of the catalyst concentrations on the rate of polymerization of 4MP1 is given in Tables IV and V. The rate of polymerization was found to be proportional to the square root of the concentration of the catalyst. The poly(4MP1) with maximum molecular weight was obtained at a particular catalyst concentration, above and below which only low molecular weight polymers were obtained. This is probably due to chain transfer to the excess triethyl aluminum present at lower catalyst concentrations or to the excess catalyst itself at higher concentrations.[13] The square root dependence was attributed to bimolecular termination, which is typical of free-radical polymerization. This is observed in the polymerization of styrene by $Cr(acac)_3$-$AlEt_3$ system,[27] of ethylene by $Cr(acac)_3$-$AlEt_3$ system,[28] and of methyl

TABLE VI
Effect of Monomer Concentration on the Rate of Polymerization and Molecular Weight of the Polymer[a]

[4MP1] (mol L^{-1})	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]				Molecular weight $\times 10^{-2}$			
	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co
0.5	0.84	0.72	0.90	0.89	66	64	69	62
1.0	1.65	1.47	1.83	1.80	69	69	73	67
1.5	2.60	2.27	2.70	2.75	77	72	75	68
2.0	3.32	3.06	3.79	3.71	84	78	82	74
2.5	4.14	3.62	4.51	4.63	89	87	87	78

[a] Conditions: reaction time = 4 h, other conditions as in Table I.
[b] R_p is determined as in Table I.

Catalyst system	[Hydroquinone] (mol L^{-1})	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]	Intrinsic viscosity (dL g^{-1})
$Cr(acac)_3$-$AlEt_3$	—	2.62	0.2525
	0.005	0.89	0.3112
$Mn(acac)_3$-$AlEt_3$	—	3.21	0.2489
	0.005	1.11	0.3014
$Fe(acac)_3$-$AlEt_3$	—	3.54	0.2618
	0.005	1.04	0.2954
$Co(acac)_3$-$AlEt_3$	—	3.59	0.2566
	0.005	1.24	0.3102

[a] Conditions: reaction time = 4 h, other conditions as in Table I.
[b] R_p is determined as in Table I.

methacrylate by $Cr(acac)_3$-$Al(isobutyl)_3$ system,[29] as well as with the catalyst systems containing acetyl acetonates of Mn, Fe, and Co with triethyl aluminum cocatalyst.[25]

Effect of monomer concentration

The rate of polymerization of 4MP1 is directly proportional to monomer concentration with all the catalyst systems employed. The molecular weights of the polymer increased with increasing concentration of the monomer (Table VI). The first-order dependence of the rate of polymerization and the linear dependence of molecular weights on the monomer indicate that the monomer does not take part in the chain transfer and the polymerization proceeds through a free-radical mechanism.[25,29] To establish the free-radical mechanism, the polymerization inhibitor hydroquinone was added to the reaction system. The rate of polymerization was reduced under the experimental conditions, thus confirming the presence of free radicals in the reaction system (Table VII).

Effect of temperature

To calculate the activation energies, the polymerization of 4MP1 was carried out at various temperatures with all the catalyst systems. The logarithms of the rates of polymerization are plotted against the reciprocals of the absolute temperature [Fig. 1 (a, b)]. The molecular weights of the polymers obtained increased regularly with temperature (Table VIII). The activation energies were found to be 30.44, 25.27, 33.51, and 29.30 kJ mol^{-1} for the catalysts with metals Cr, Mn, Fe, and Co, respectively. Similar activation energy values were obtained in the polymerization of methyl methacrylate with $Cr(acac)_3$-$Al(isobutyl)_3$,[29] and of methyl methacrylate and styrene with $CuCl_2$-$AlEt_3$ catalyst systems,[30,31] wherein a free-radical mechanism was proposed.

Reaction mechanism and kinetic scheme

Based on all the experimental results described previously and taking into consideration the consensus of published information, a probable mechanism is proposed as follows, which is in agreement with the experimental results:
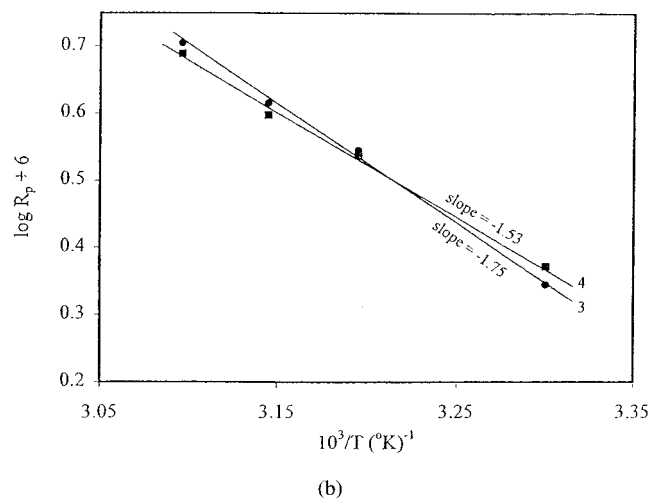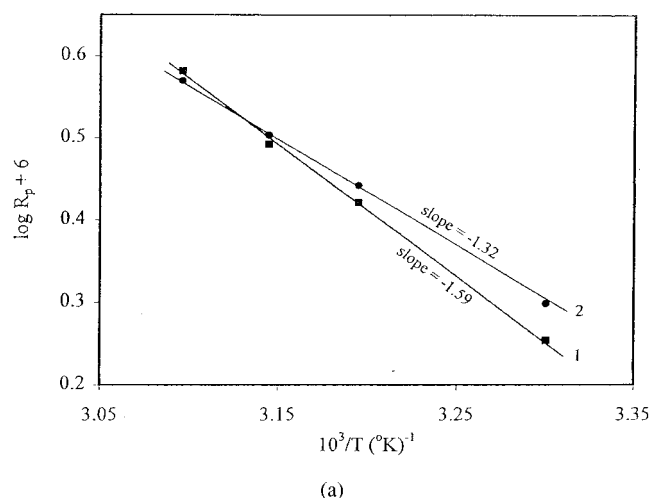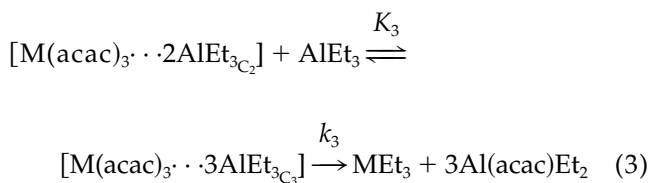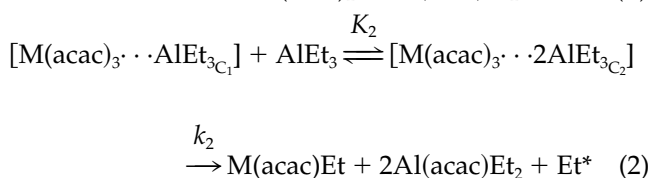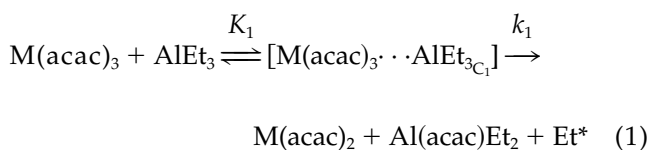

(a)

(b)

Figure 1 (a) Arrhenius plots for the polymerization of 4-methylpentene-1 with the catalyst systems $Cr(acac)_3$-$AlEt_3$ (1) and $Mn(acac)_3$-$AlEt_3$ (2). (b) Arrhenius plots for the polymerization of 4-methylpentene-1 with the catalyst systems $Fe(acac)_3$-$AlEt_3$ (3) and $Co(acac)_3$-$AlEt_3$ (4).

TABLE VIII
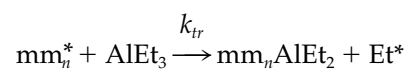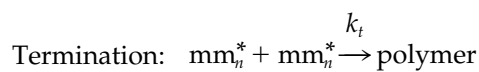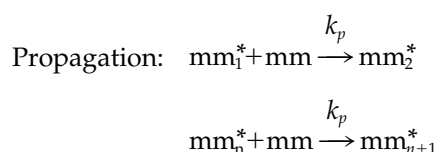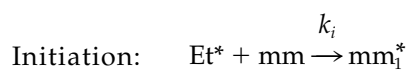**Effect of Temperature on the Rate of Polymerization and Molecular Weight of the Polymer[a]**

Temperature (°C)	$R_p \times 10^6$ (mol L^{-1} s^{-1})[b]				Molecular weight $\times 10^{-2}$			
	Cr	Mn	Fe	Co	Cr	Mn	Fe	Co
30	1.79	1.99	2.21	2.35	63	72	74	60
40	2.64	2.77	3.51	3.44	65	77	83	66
45	3.11	3.19	4.13	3.96	71	84	85	68
50	3.82	3.72	5.07	4.89	77	87	89	72

[a] Conditions: reaction time = 4 h, other conditions as in Table I.
[b] R_p is determined as in Table I.

$$\text{M(acac)}_3 + \text{AlEt}_3 \underset{K_1}{\rightleftharpoons} [\text{M(acac)}_3 \cdots \text{AlEt}_{3_{C_1}}] \xrightarrow{k_1}$$

$$\text{M(acac)}_2 + \text{Al(acac)Et}_2 + \text{Et*} \quad (1)$$

$$[\text{M(acac)}_3 \cdots \text{AlEt}_{3_{C_1}}] + \text{AlEt}_3 \underset{K_2}{\rightleftharpoons} [\text{M(acac)}_3 \cdots 2\text{AlEt}_{3_{C_2}}]$$

$$\xrightarrow{k_2} \text{M(acac)Et} + 2\text{Al(acac)Et}_2 + \text{Et*} \quad (2)$$

$$[\text{M(acac)}_3 \cdots 2\text{AlEt}_{3_{C_2}}] + \text{AlEt}_3 \underset{K_3}{\rightleftharpoons}$$

$$[\text{M(acac)}_3 \cdots 3\text{AlEt}_{3_{C_3}}] \xrightarrow{k_3} \text{MEt}_3 + 3\text{Al(acac)Et}_2 \quad (3)$$

where $M = \text{Cr, Mn, Fe, Co, and}$

Initiation: $\text{Et*} + \text{mm} \xrightarrow{k_i} \text{mm}_1^*$

Propagation: $\text{mm}_1^* + \text{mm} \xrightarrow{k_p} \text{mm}_2^*$

$$\text{mm}_n^* + \text{mm} \xrightarrow{k_p} \text{mm}_{n+1}^*$$

Termination: $\text{mm}_n^* + \text{mm}_n^* \xrightarrow{k_t} \text{polymer}$

$$\text{mm}_n^* + \text{AlEt}_3 \xrightarrow{k_{tr}} \text{mm}_n\text{AlEt}_2 + \text{Et*}$$

Applying a steady-state principle for the radical mm_n^*

$$d[\text{mm}_n^*]/dt = k_i[\text{Et*}][\text{mm}] - k_t[\text{mm}_n^*]^2$$

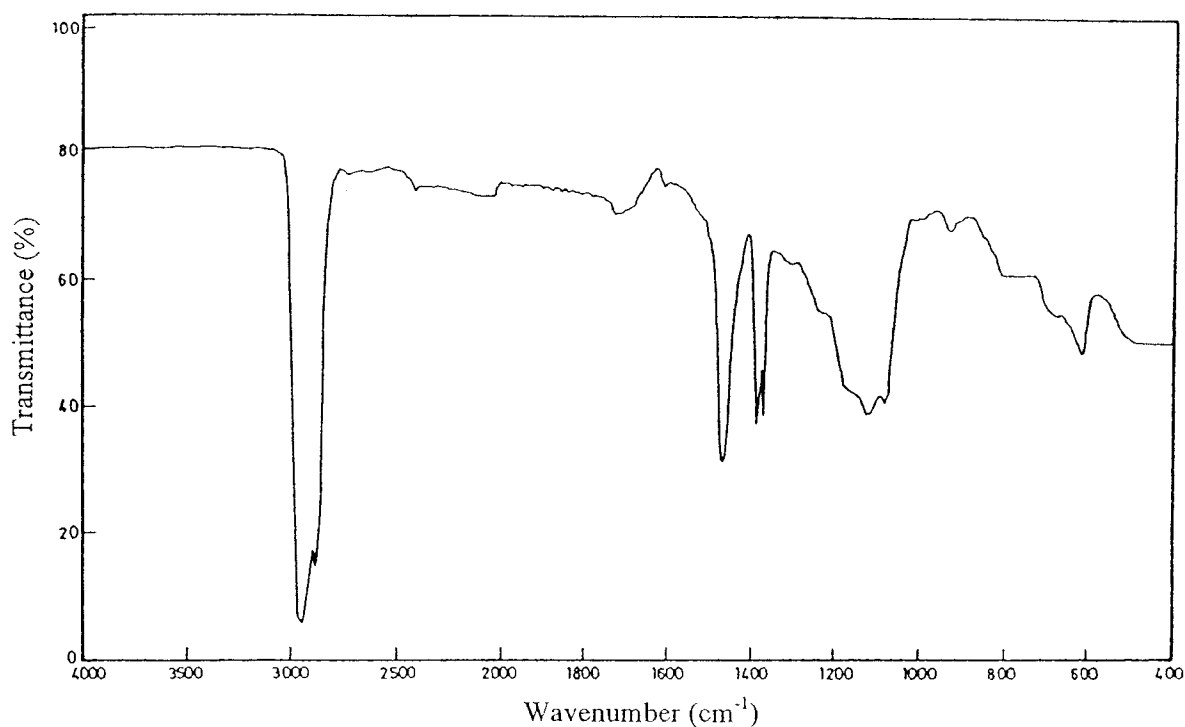$$- k_{tr}[\text{mm}_n^*][\text{AlEt}_3] = 0 \quad (4)$$

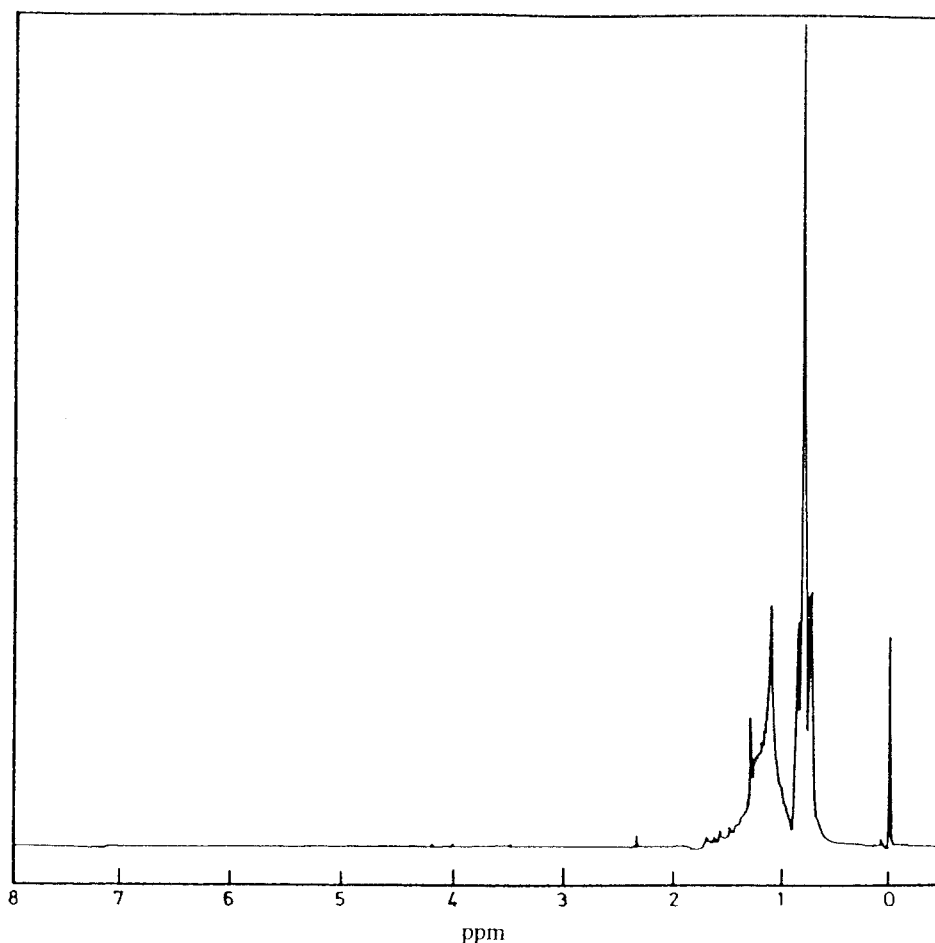**Figure 2** IR spectrum of poly(4-methylpentene-1).

Figure 3 ^{1}H-NMR spectrum of poly(4-methylpentene-1).

Applying steady state principle for the radical Et^*

$$d[Et^*]/dt = k_1[C_1] + k_2[C_2] - k_i[Et^*][mm]$$
$$+ k_{tr}[mm_n^*][AlEt_3] = 0 \quad (5)$$

$$k_i[Et^*][mm] = k_1[C_1] + k_2[C_2] + k_{tr}[mm_n^*][AlEt_3] \quad (6)$$

Substituting eq. 6 in eq. 4,

$$d[mm_n^*]/dt = k_1[C_1] + k_2[C_2] - k_t[mm_n^*]^2 = 0 \quad (7)$$

After rearranging eq. 7,

$$[mm_n^*] = \frac{(k_1[C_1] + k_2[C_2])^{1/2}}{k_t^{1/2}} \quad (8)$$

Because

$$C_1 = K_1[M(acac)_3][AlEt_3] \quad (9)$$

$$C_2 = K_1K_2[M(acac)_3][AlEt_3]^2 \quad (10)$$

Substituting eqs. 9 and 10 in eq. 8,

$$[mm^*] = (k_1K_1[M(acac)_3][AlEt_3]$$
$$\frac{+ k_2K_1K_2[M(acac)_3][AlEt_3]^2)^{1/2}}{k_t^{1/2}} \quad (11)$$

The rate of polymerization,

$$R_p = k_p[mm_n^*][mm] \quad (12)$$

Substituting eq. 11 in eq. 12,

$$R_p = k_p[mm] \frac{(k_1K_1[M(acac)_3][AlEt_3]}{\displaystyle + k_2K_1K_2[M(acac)_3][AlEt_3]^2)^{1/2}}{k_t^{1/2}}$$

or

$$R_p = k_p[mm] \frac{[M(acac)_3]^{1/2}[AlEt_3]^{1/2}}{k_t^{1/2}}$$
$$\times (k_1K_1 + k_2K_1K_2[AlEt_3])^{1/2}$$

Hence, order with respect to $[mm] = 1.0$; order with respect to $[M(acac)_3] = 0.5$; and order with respect to $[AlEt_3] = 0.5 \rightarrow 1.0$.
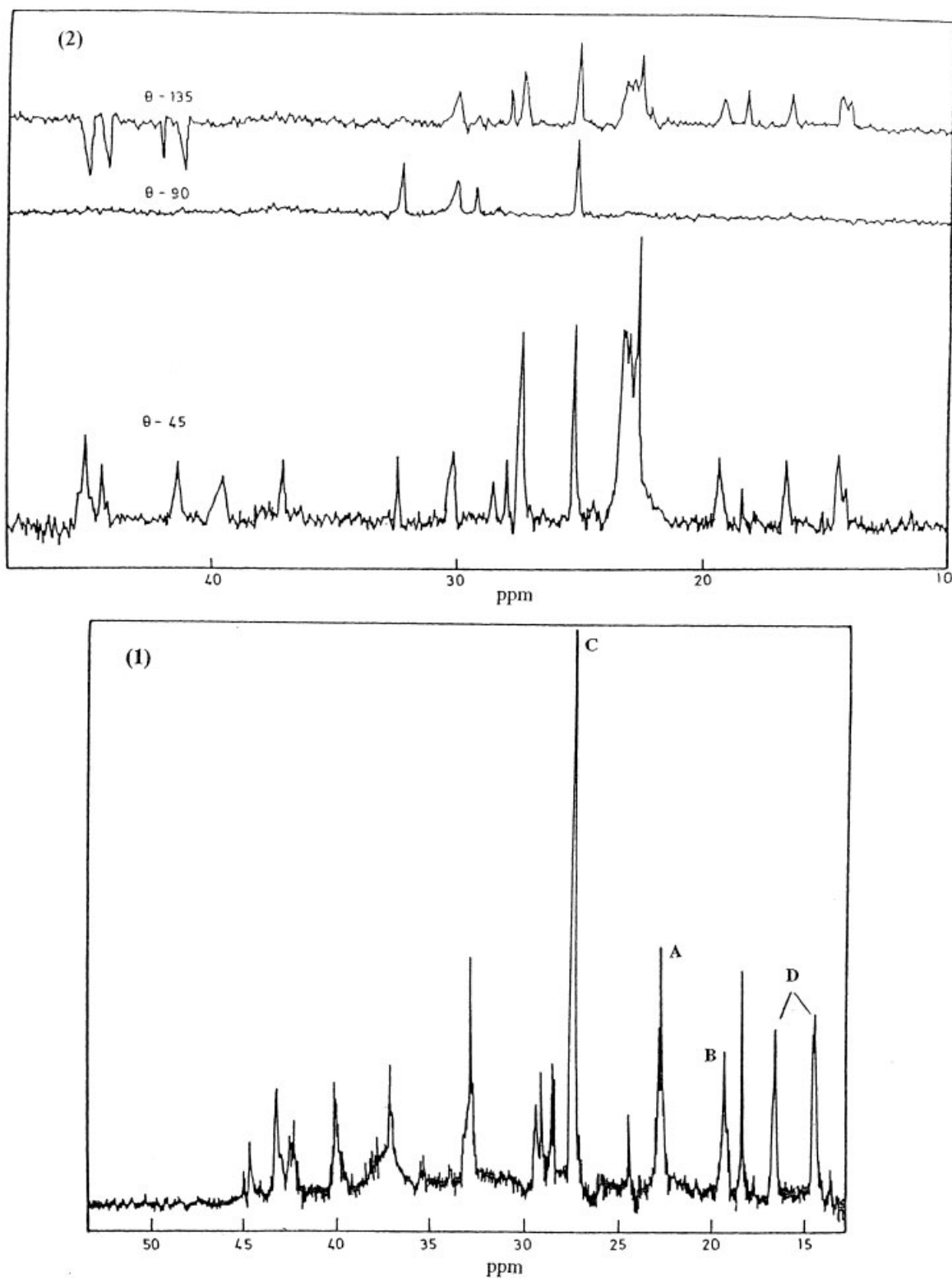
Figure 4 ^{13}C-NMR spectrum (1) and ^{1}H-decoupled ^{13}C-DEPT spectra (2) of poly(4-methylpentene-1).

At very high concentrations of the cocatalyst (i.e., Al/M > 2.0), complex C_3 is formed, thus reducing C_1 and C_2, thereby decreasing the rate.

Polymer characterization

Because the spectral features of the polymer products obtained by using all the catalyst systems are almost identical, for each technique, the representative data of the polymer prepared using the catalyst system Cr(a-cac)$_3$-AlEt$_3$ are given.

IR spectroscopy

The IR spectrum of poly(4MP1) is given in Figure 2. The sharp intense band at 2920–2960 cm^{-1} is attrib-
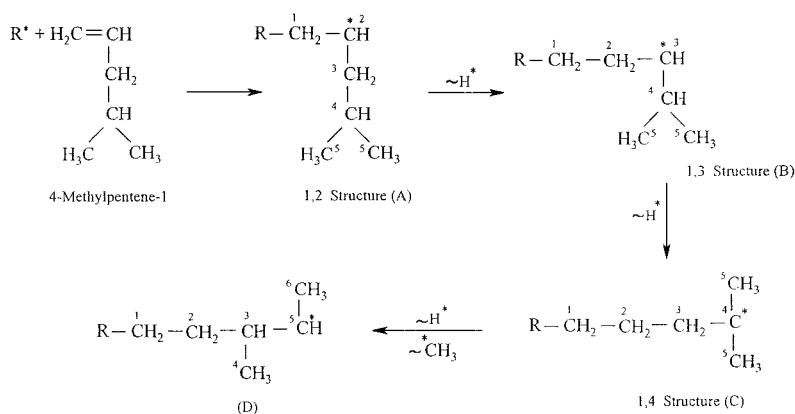
Scheme 1 Mechanism of formation of different structural units.

uted to the C—H stretching vibrations and at 1465 cm^{-1} is due to the C—H bending vibrations of the methylene and methyl groups, respectively. A doublet with equal intensity at 1385 and 1370 cm^{-1} is due to the isopropyl group of the polymer. The disappearance of C=C stretching vibration at 1640 cm^{-1} explains the formation of poly(4MP1).

^{1}H-NMR spectroscopy

The ^{1}H-NMR spectrum of poly(4MP1) is shown in Figure 3. It is seen that the signals are overlapping and fall below 2 ppm. The three signals at 0.8, 1.2, and 1.6 ppm are attributed to methyl, methylene, and methine protons, respectively. The absence of signals between 5 and 6 ppm clearly indicates the disappearance of the double bond during the polymerization. Splitting of methyl signals is observed that gives evidence for the formation of rearranged units during the course of polymerization. However, the precise determination of the structures of the rearranged units is difficult because of the overlapping of the signals.

^{13}C-NMR spectroscopy

The ^{13}C-NMR spectrum of poly(4MP1) is shown in Figure 4, the features of which are essentially the same as those reported in the literature wherein the isomerized polymeric structures of 4MP1 have been identified through the cationic polymerization.[32–34] The formation of these structures through hydride and methide shifts is given in Scheme 1(A–D). To distinguish

the types of carbon species, ^{13}C-NMR spectrum of the polymer was also measured through the ^{1}H-decoupled DEPT mode at $\theta = 45°$, 90°, and 135°, which is presented in Figure 4 together with the ordinary spectrum (upward signal: CH, CH$_3$; downward signal: CH$_2$). The peaks at 22.4, 19.0, 27.3, and 16.3/14.5 ppm are assigned to the methyl groups of units A, B, C, and D, respectively, which are accordingly marked in Figure 4. The various peak values for all the isomerized structures are assembled in Table IX. The contents of the units A–D were determined from the relative peak areas of methyl groups according to the procedure adopted by Ferraris et al.[33] and are given in Table X for the formation of polymers with different catalyst systems.

In all the cases, 1,4-structure (C) is predominant, which conforms to the reports wherein the poly(4MP1) was prepared through cationic polymerization in polar solvent.[33,34] Contrarily, the same polymer when prepared under identical conditions in nonpolar solvents gave the mixture of isomerized products in different proportions with structures C and D in almost equal amounts.[33] This difference in structure has been attributed to the existence of the chain propagating centers as paired ions, which hinders the double hydride shift necessary for the formation of structural unit C because of intimate contact of the counterion with the growing carbenium ion. Because in the present case the polymerization proceeds through a free-radical mechanism, the double hydride shift can be expected to proceed without any such hindrance for the formation of structure C in a

TABLE IX
Peak Values for Various Carbon Species
in the Isomerized Polymeric Structures

| Structure | Chemical shift from TMS (ppm) | | | | | |
	C^1	C^2	C^3	C^4	C^5	C^6
A	41.4	30.3	45.0	24.8	22.4	—
B	29.3	29.3	43.7	29.1	19.0	—
C	43.3	18.4	43.3	33.0	27.3	—
D	33.1	31.0	38.5	14.5	39.5	16.3

TABLE X
Amounts of Structural Units with Various Catalyst
Systems Under Study Calculated from ^{13}C-NMR Spectra

| Catalyst system | % Conversion | Structural units (%) | | | |
		A	B	C	D
Cr(acac)$_3$-AlEt$_3$	3.86	23.0	10.4	52.0	14.6
Mn(acac)$_3$-AlEt$_3$	3.40	24.4	17.1	46.3	12.2
Fe(acac)$_3$-AlEt$_3$	3.71	18.2	18.2	56.8	6.8
Co(acac)$_3$-AlEt$_3$	3.97	28.0	17.1	41.5	13.4

higher proportion. The presence of 1,2-structure (A) is consistent with the previous reports.[32,33] However, Mizuno and Kawachi[34] did not observe this isomer in the product prepared through cationic polymerization in polar medium. They obtained downward signals at 22.1 and 24.7 ppm in the DEPT spectrum, which they attributed to the methylene groups at position two (^{2}C) of the isomers B and C in the triad structures —B—C—B— (or) —D—C—B— and —C—B—B—, respectively. In the present investigation, no such downward signals are observed.

CONCLUSION

The kinetic study carried out on the polymerization of 4-methylpentene-1 with soluble, homogenous Ziegler–Natta-type catalyst systems, $M(acac)_3$-AlEt$_3$ (M = Cr, Mn, Fe, and Co), in benzene medium reveals first-order dependence on monomer and order of 0.5 with respect to catalyst concentration. Through the kinetic data obtained, a free-radical mechanism is proposed. For all the catalyst systems, polymerization yields isomerized polymeric structures with 1,4-structure as dominant.

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