Journal of Macromolecular Science, Part A

Quaterpolymerization of Ethylene, Propylene, Dicyclopentadiene, and Methylcyclopentadienyl-5-endo-norborn-2-enyl-methane

S. Cesca[a]; S. Arrighetti[a]; G. Bertolini[a]; M. Bruzzone[a]

[a] SNAM PROGETTI S.p.A. Polymer Research Laboratories, San Donato, Milanese, Italy

PLEASE SCROLL DOWN FOR ARTICLE

Quaterpolymerization of Ethylene, Propylene, Dicyclopentadiene, and Methylcyclopentadienyl-5-endo-norborn-2-enyl-methane

S. CESCA, S. ARRIGHETTI, G. BERTOLINI, AND M. BRUZZONE

SNAM PROGETTI S.p.A.
Polymer Research Laboratories
San Donato Milanese, 20097, Italy

ABSTRACT

The quaterpolymerization of methylcyclopentadienyl-5-endo-norborn-2-enyl-methane with ethylene, propylene, and either endo- or exo-dicyclopentadiene was studied by using the catalyst system $VAcac_3$-Et_2AlCl. The influence of catalyst and polyenes concentrations, catalyst modifiers, and other polymerization parameters on the general properties of quaterpolymers was investigated. The polymers obtained showed a random distribution of the comonomeric units and the ability to covulcanize with 1,4-cis-polyisoprene.

INTRODUCTION

While the terpolymerization of endo-dicyclopentadiene (I), i.e., the usual stereoisomeric form of the dimer of cyclopentadiene [1] with ethylene and propylene, has been studied extensively in the past 15 years [2-9], only recently has the terpolymer based on exo-dicyclopentadiene (II) [10] or methylcyclopentadienyl-5-endo-norborn-2-enyl-methane (III) been described [11].

(I)   (II)   (III)
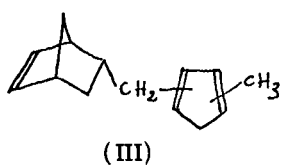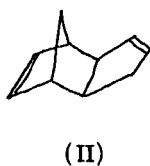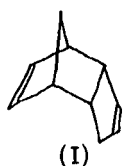
Many papers have been devoted to terpolymers containing different dienes (EPDM) or trienes (EPTM) [12], but no reports on quaterpolymers containing two α-olefins and two polyenes can be found in the literature. Only a brief mention exists [13] concerning the comparison of some vulcanizate properties of mixtures of EPDMs based on two different dienes and the corresponding quaterpolymer. However, no data have been presented about the synthesis and the main properties of the multicomponent polymeric system studied from the prevailing technological point of view [13].

Recently, a detailed study of quaterpolymers containing acrylic esters as comonomeric units, besides ethylene, propylene, and endo-dicyclopentadiene, has been published [14]. A high utilization of the acrylic monomers and a reduced interference of them with the catalytic species has been observed, provided that the ester groups are complexed with a Lewis acid before contacting coordinate catalysts which, however, yield random distribution of four comonomers.

This paper describes quaterpolymers based on both I-III and II-III.

EXPERIMENTAL

Materials

Ethylene, propylene, solvents, Lewis bases, catalyst components, and other reagents had the same origin and were subjected to the same preliminary treatment as previously reported [15-17]. Diene I was a commercial product, fractionally distilled twice before use [18]; Diene II was prepared as reported elsewhere [19], while Triene III was described previously [11].

Polymerization

The procedure adopted was the same as reported in the case of terpolymerization studies [10, 14].

Analyses

UV, IR, NMR, and VPC measurements were carried out as described elsewhere [20].

The content of III was obtained from UV measurements which had been compared previously [11] with the radiochemical dosage of EPTM containing tritium labeled III, while the dosage of I or II was deduced from careful ICl absorption [21], tested also on III-EPTM, after subtracting the datum of UV measurement obtained on the same sample.

$\overline{M}_n$, intrinsic viscosity, and fractionation data were obtained as described previously [11].

RESULTS AND DISCUSSION

Quaterpolymers Containing I and III

The catalyst used in these investigations was $VAcac_3-Et_2AlCl$ which had been employed as an unaged system during the synthesis of some EPTMs [10, 11, 15, 17].

A linear relationship has been found between the average quaterpolymerization rate and the catalyst concentration (Figs. 1A and 1B) as it occurs for the corresponding terpolymerization processes based on I (Fig. 1C) and III (Fig. 1D). The data of Fig. 1 have been obtained maintaining a constant overall concentration of I and varying that of III (Fig. 1A), or vice versa (Fig. 1B). However, all the data of Fig. 1 are quite similar and show an efficient poison action exerted by both the polyenes used. The influence of the concentration of Triene III on quaterpolymer yield is more evident in Fig. 2, while Fig. 3 indicates that Diene I is fivefold less poisonous than III at the same polyene concentration.

When constant yields of polymer are considered, it is conceivable that increasing amounts of catalyst are required as soon as the concentration of I or III in the feed increases. However, the quaterpolymer is obtained with a consumption of catalyst which is, within experimental error, higher than the sum of catalyst consumption of single terpolymers (Fig. 4). The explanation of such a result is not immediate on the basis of the data so far collected.

The yield of polymer influences the content of III in quaterpolymer at the different levels of triene investigated (Fig. 5), whereas the content of I is independent of both the polymer yield and the concentration of III. Similar dependences have been observed for III-EPTM; the results should be attributed to the low concentration of Triene III with respect to the other participants in the reaction.

The introduction of III in quaterpolymer chains is proportional to the concentration of triene in the feed (Fig. 6), similar to what has been observed in the corresponding EPTM (Fig. 7). The comparison of Figs. 6 and 7, where the different lines refer to different yields of
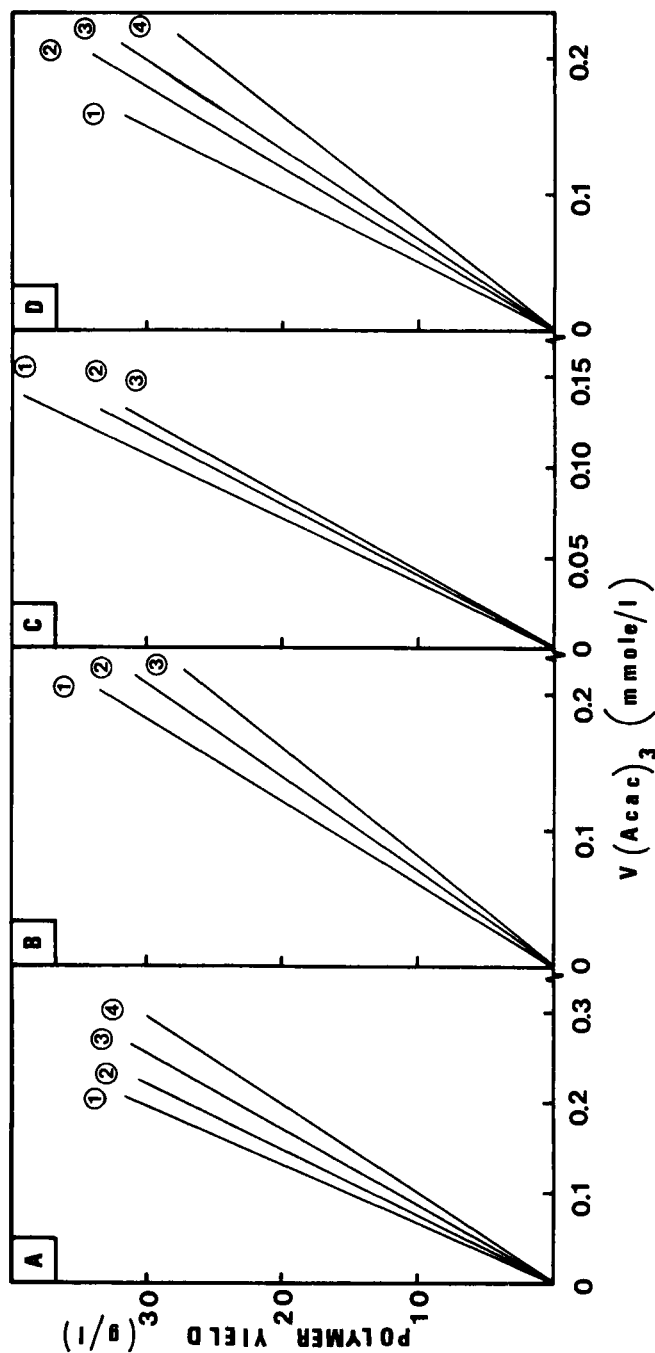
FIG. 1. Dependence of polymer yield on catalyst concentration. Conditions: solvent, toluene; $Et_2AlCl/VAcac_3 = 8.0$; molar ratio in the gaseous stream $C_3H_6/C_2H_4 = 2.0$; time, 20 min. (A): $I = 17.3$ mmoles/liter; III: (1) = 5.4, (2) = 7.2, (3) = 9.0, and (4) = 13.6 mmoles/liter. (B): III = 5.1 mmoles/liter; I: (1) = 17.3, (2) = 23.1, and (3) = 30.8 mmoles/liter. (C): I: (1) = 17.3, (2) = 23.1, and (3) = 34.6 mmoles/liter. (D): III: (1) = 5.4, (2) = 7.2, (3) = 9.0, and (4) = 13.6 mmoles/liter.

FIG. 2. Influence of triene III concentration on quaterpolymer yield. Conditions as in Fig. 1. I = 17.3 mmoles/liter; VAcac$_3$: (1) = 0.10, (2) = 0.15, and (3) = 0.20 mmole/liter.
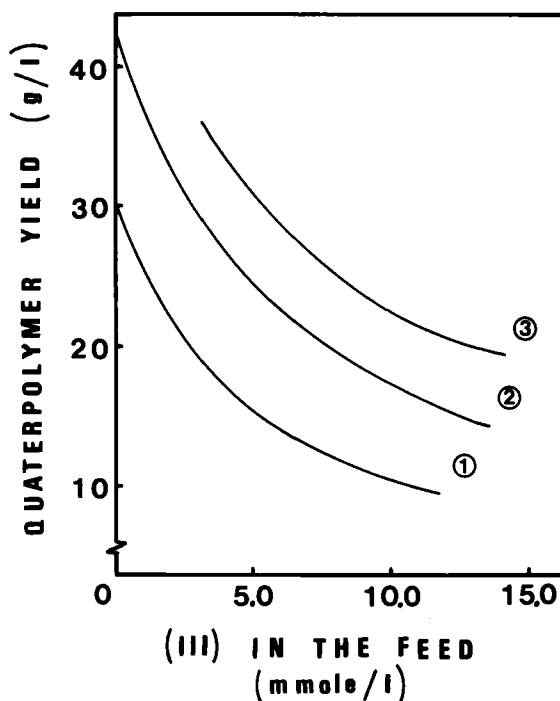
polymer, allows confirmation of the negative influence exerted by I on the degree of insertion of III into polymer chains. The result can be explained on the basis of current views, according to which the action mechanism of coordinate polymerization is depicted [12]. The simultaneous presence of two polyenes in the reaction medium influences their coordination to catalyst centers because both of them compete for bonding to active species, and the final result is the reduction of the concentration in the polymer of one polyene when the other is present. Figure 8 confirms such an interpretation. The mild influence of I agrees with a lower coordinate ability of the diene with respect to III which possesses a system of two conjugated double bonds.

Under the conditions adopted, the content of I in the quaterpolymer is proportional to the diene concentration in the feed (Fig. 9), while the well-known action of chain transfer exerted by the metallorganic
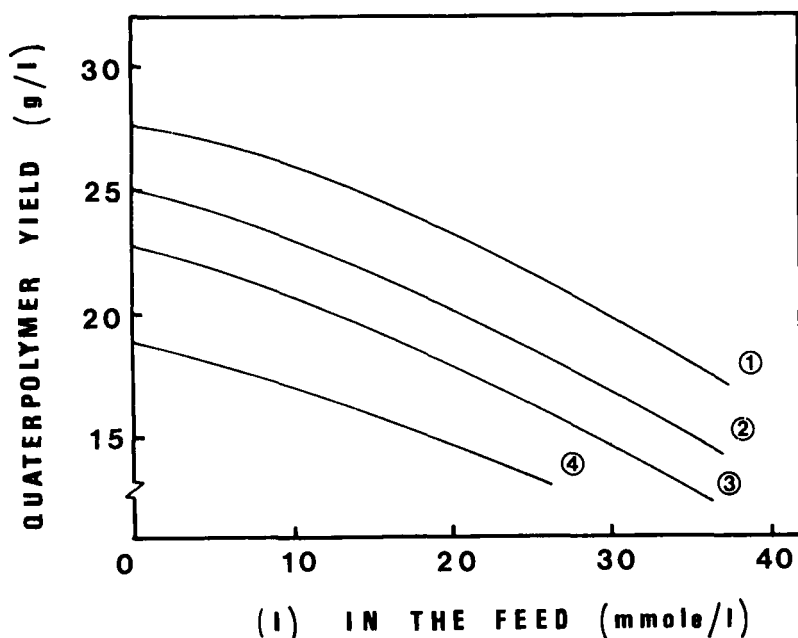
FIG. 3. Influence of diene I concentration on quaterpolymer yield. Conditions as in Fig. 1. $VAcac_3$ = 0.15 mmole/liter; III: (1) = 5.4, (2) = 7.2, (3) = 9.0, and (4) = 13.6 mmoles/liter.

component of Ziegler-Natta systems [22] is detectable in the case of both ter- and quaterpolymers based on I and III (Figs. 10, 11, and Ref. 11). Furthermore, the polyenes used in this work also exert a chain-breaking action which is proportional to their concentration.

Several Lewis bases have been added to coordination catalysts used for homopolymerization [23] and terpolymerization [11, 16] of α-olefins, but the explanation of their action mechanism is quite unsatisfactory since it is essentially qualitative and sometimes contradictory results have been obtained [23].

Three Lewis bases, pyridine, $P(C_6H_5)_3$, and $P(n-C_4H_9)_3$, have been added separately to the complex system of quaterpolymerization based on I and III; the base was added to the polyenes solution and introduced continuously in the feed during the polymerization time. The findings obtained confirm in part the result previously obtained [10] during the III-EPTM synthesis, i.e., electron donors reduce the number of catalyst centers proportionally to their basic strength (Fig. 12), while the utilization of I and III is practically the same as in the absence of any base.
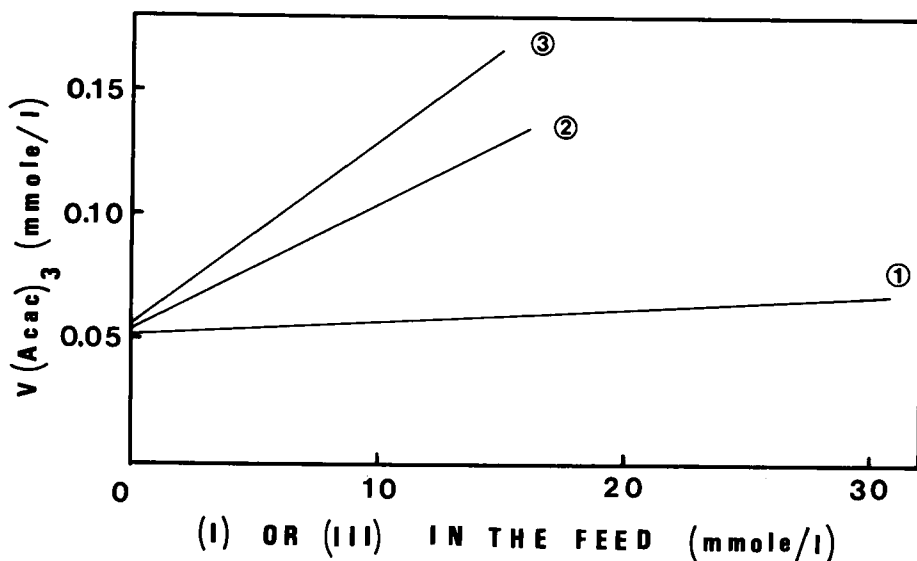
FIG. 4. Dependence of catalyst consumption at constant polymer yield (i.e., 15 g/liter) on the polyene(s) concentration. (1): I-based EPDM. (2): III-based EPTM. (3): Quaterpolymer based on the same levels of I and III as in (1) and (2).

The presence of C_5H_5N(Py) or $P(C_6H_5)_3$ yields quaterpolymers which show a small but significant increase of $[\eta]$ values with respect to the products obtained without donors (Fig. 13). A similar effect, much more enhanced, was detected in the case of III-EPTM when anisole and triethylamine were used, but not in the case of Py [11]. Tentatively the result was attributed to the ability of Lewis bases to disproportionate alkylaluminum halides into acidic products which become bonded to the base [24] and might be able to promote side reactions involving the unsaturation of the polymer [11]. An increase of MW, up to gel formation, could be the final result.

Apparently the behavior of Py is not the same in a ter- or quaterpolymerization system; similarly, there is a clear difference between $P(C_6H_5)_3$ and $P(n\text{-}Bu)_3$ in the quaterpolymerization process (Fig. 13). One would be tempted to invoke a specific role for aromatic rings in the complex picture of concurrent equilibrium reactions in which catalyst components, monomers, and every nucleophilic molecule are involved, but in the absence of specific data referring to individual steps of the overall process, an adequate comment is impossible.
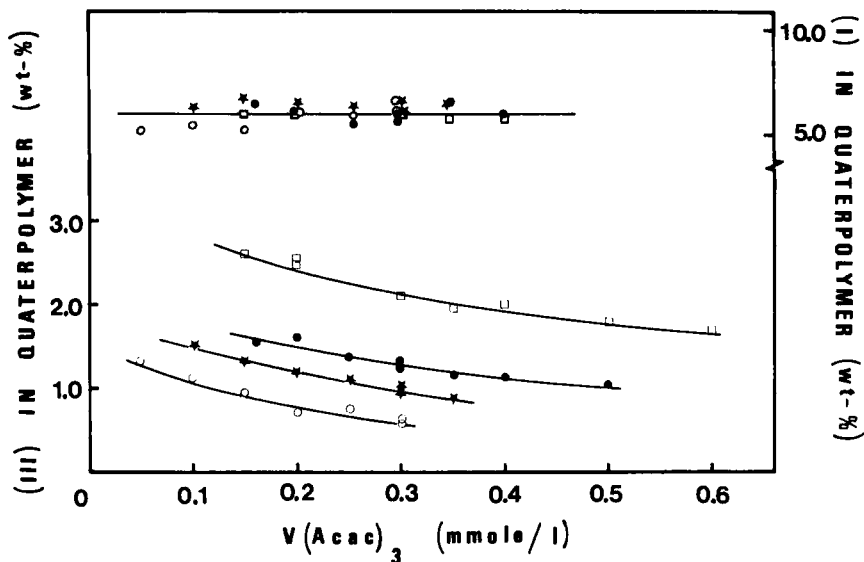
FIG. 5. Influence of catalyst concentration on the content of polyenes in quaterpolymer. III: (○) = 5.4, (★) = 7.2, (●) = 9.0 and (□) = 13.6 mmoles/liter in the feed. Other conditions as in Fig. 1.

Quaterpolymers Containing (II) and (III)

In a previous paper we described and discussed the IR characteristics of EPDM based on II in comparison with the spectral data obtained from I-EPDM [9]. The interesting behavior of terpolymer containing II during the vulcanization process has been evidenced and quantitatively determined in another paper [25] on the basis of a kinetic scheme which takes into account both the cross-linking reactions and the reverse processes. Furthermore, it has been ascertained that the presence of norbornenic termonomers having the substituent group which carries the secondary unsaturation in the exo configuration imparts to EPDM a higher vulcanization rate with respect to terpolymer based on the same ter-monomer with endo configuration.

Analogous differences have been found for other types of reactions including exo and endo derivatives of norbornene [26] and the cyclohexene [27] series. Torsional angle effects (eclipsing strain energy) have been invoked, instead of remote steric effects, to account for the stereochemistry of attack of some reagents on the aforecited structures.

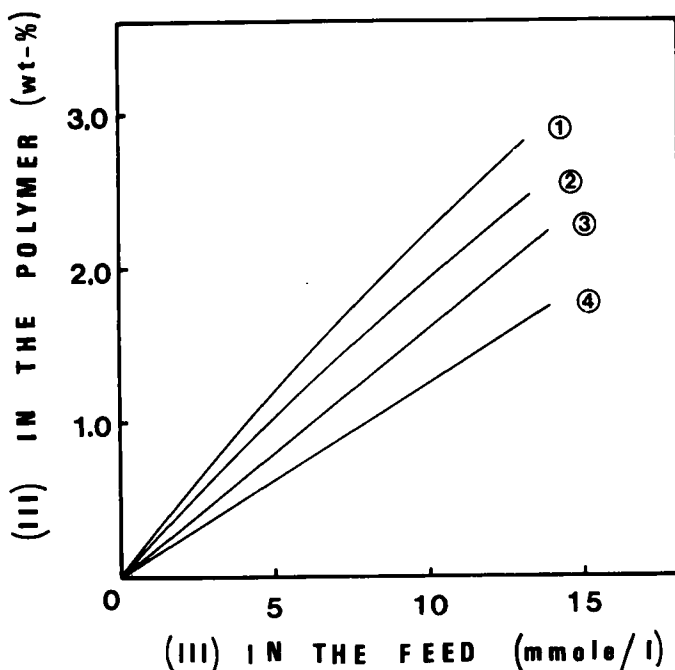In this paper we also report on some preliminary data concerning

FIG. 6. Relationship between concentration of III in the feed and its content in quaterpolymer. Conditions as in Fig. 1; I = 17.3 mmoles/liter. Curves obtained at constant yield: (1) = 10, (2) = 20, (3) = 30, and (4) = 40 g/liter of polymer.

the synthesis of quaterpolymers based on II and III. As shown in Fig. 14, once again there is a first-order dependence of the average polymer-ization rate on the catalyst concentration, while MWs of the resulting quaterpolymer are makedly influenced by the polymerization tempera-ture and the catalyst concentration.

It is worth noting that the content of II depends significantly on VAcac$_3$ concentration as a consequence of the enhanced reactivity of II in the polymerization stage [28] (Fig. 15). Furthermore, it is confirmed [12] that when the polymerization temperature is lowered, the polyene utilization decreases, whereas the MW increases.

The influence of the concentration of III on the quaterpolymer yield is relatively low when the content of II is constant, while it is more signif-icant on MW (Fig. 16). However, the flattening of the diagram of Fig. 16, with respect to Fig. 2, should be attributed to the higher con-centration of catalyst and diene used in the former experiments.

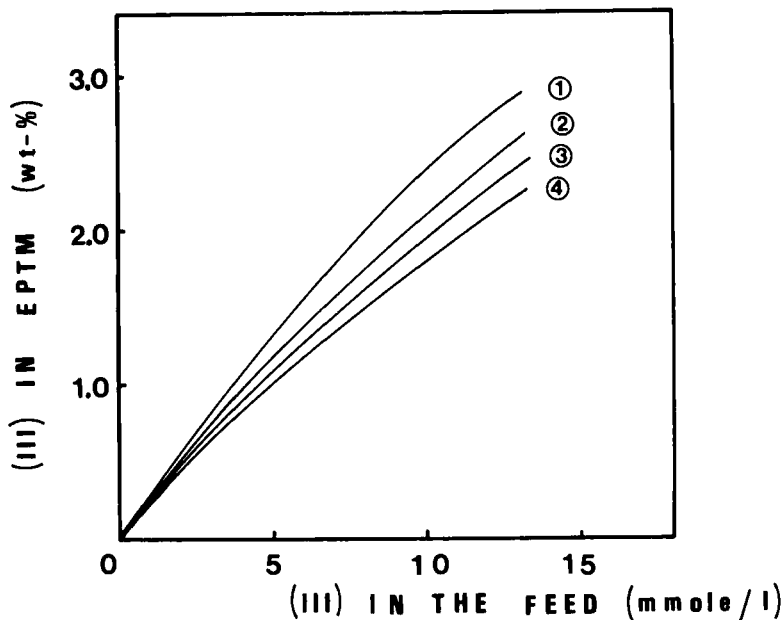The competitive action between II and III in coordinating to active

FIG. 7.   Relationship between the concentration of III in the feed and its content in EPTM.   Conditions as in Fig. 1.   Curves obtained at constant yield, as in Fig. 6.

centers is shown in Fig. 17 where the content of both the polyenes, obtained from sample of quaterpolymer produced with a constant concentration of II in the feed, is plotted against the concentration of III in the feed.

Properties of Quaterpolymers

The random distribution of the polyenes in the quaterpolymers studied in this work has been determined in the case of I and III by means of fractionation measurements (Table 1).   On the other hand, in the case of the parent terpolymers, i e., based on I and III, evidence of the statistical distribution of comonomers along the chains [5, 9, 11] has been attained.

The main results of spectroscopic investigation are collected in Table 2; the presence of III is demonstrated by the typical UV absorption at 254 mμ [11], while the presence of I or II is proved by the
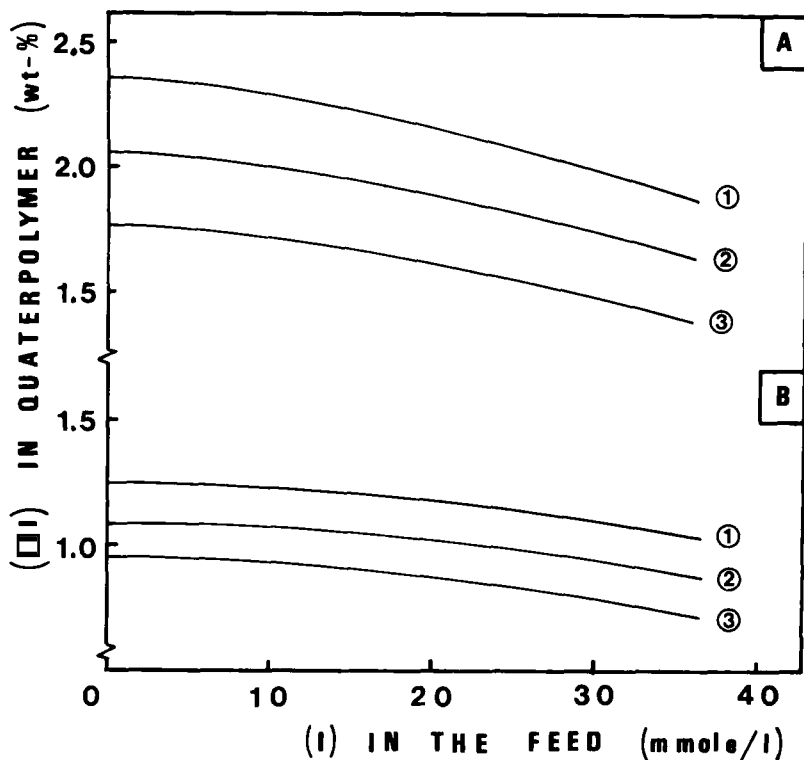
FIG. 8. Influence of the concentration of I in the feed on the content of III in the quaterpolymer. Conditions as in Fig. 1. (A): III = 10.3 mmoles/liter; (B): III = 5.1 mmoles/liter; (1) = 10, (2) = 20, and (3) = 30 g/liter of polymer.

existence of principal IR absorptions typical of the dihydro derivatives of I and II, previously investigated [10].

Some solution properties of the quaterpolymers described here are compared with the measurements obtained for terpolymers containing I, II, and III in Table 3. The presence of Polyene III significantly reduces the polydispersity of both ter- and quaterpolymer; the same influence is exerted by 1-isopropylidene-3a,4,7,7a-tetrahydroindene on the resulting EPTM [20].

The behavior in vulcanization and covulcanization experiments (with highly unsaturated elastomers) of quaterpolymers containing low amounts of III, i.e., less than 1 wt%, is excellent as has also been
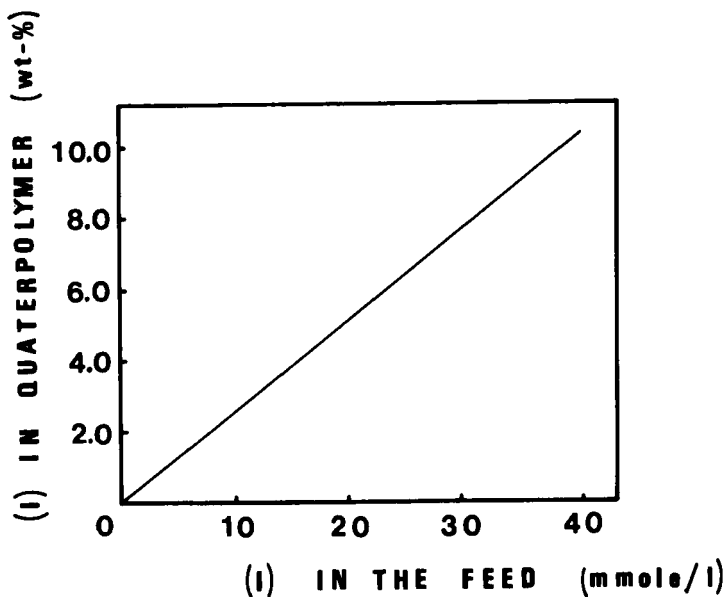
FIG. 9. Relationship between the concentration of I in the feed and its content in quaterpolymer at constant polymer yield (i.e., 30 g/liter); III = 10 mmoles/liter.

observed [12] in the case of EPTM containing the same level of Triene III. Furthermore, in the case of quaterpolymers containing I or II besides III, some tensile properties of the vulcanizates are better than for the simple EPTM based on III (Figs. 18-20).

CONCLUSIONS

The selective opening of norbornene double bonds of III, in the presence of a coordination catalyst has been confirmed in the case of quaterpolymerization experiments with ethylene, propylene, and both the stereoisomeric forms of dicyclopentadiene.

The same conclusions as were pointed out [10] in the case of EPTM based on III can be considered valid for the more complex system of quaterpolymerization which is carried out easily when the
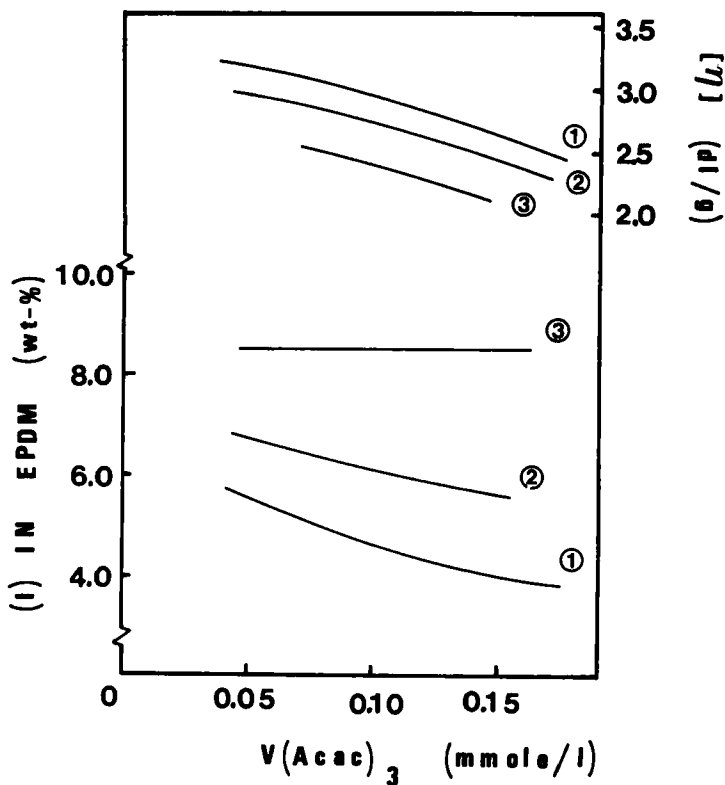
FIG. 10. Influence of catalyst and termonomer concentration on intrinsic viscosity and diene content of EPDM based on I. I: (1) = 17.3, (2) = 23.1, and (3) = 34.6 mmoles/liter.
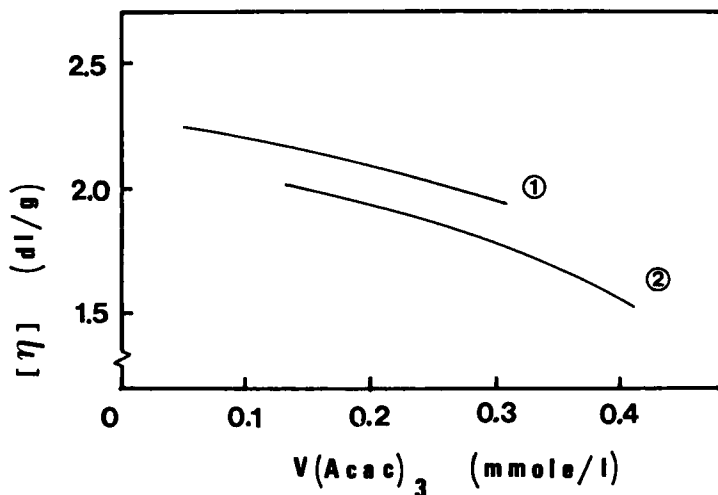

FIG. 11. Influence of catalyst and III concentration on [η] of quater-polymer. I = 17.3 mmoles/liter; III: (1) = 5.4, and (2) = 9.0 mmoles/liter.
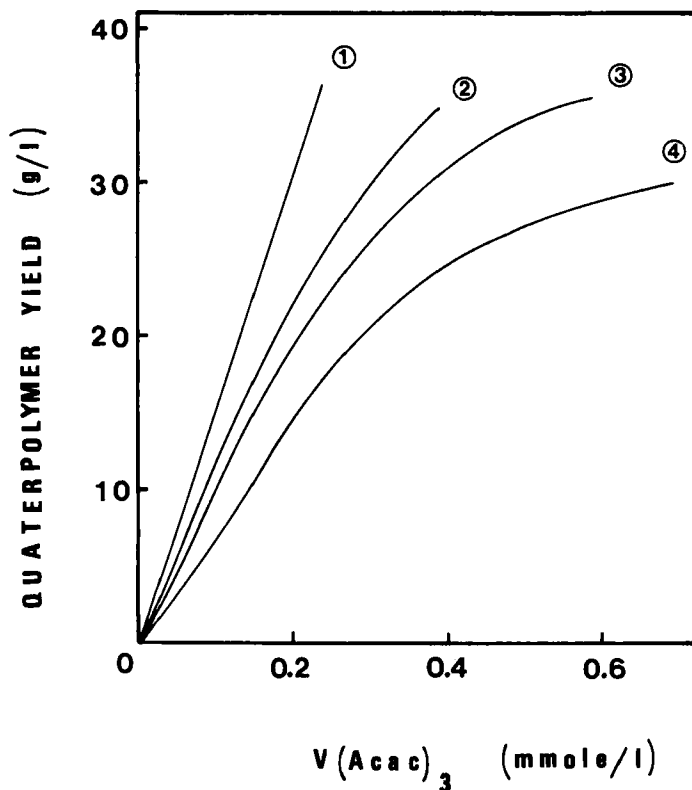
FIG. 12. Influence of some Lewis bases on quaterpolymer yield.
I = 5.8 mmoles/liter; III = 5.4 mmoles/liter; (1) = no base, (2) =
C_5H_5N, N/Al = 0.3, (3) = $P(C_6H_5)_3$, P/Al = 0.3, and (4) = $P(n-C_4H_9)_3$,
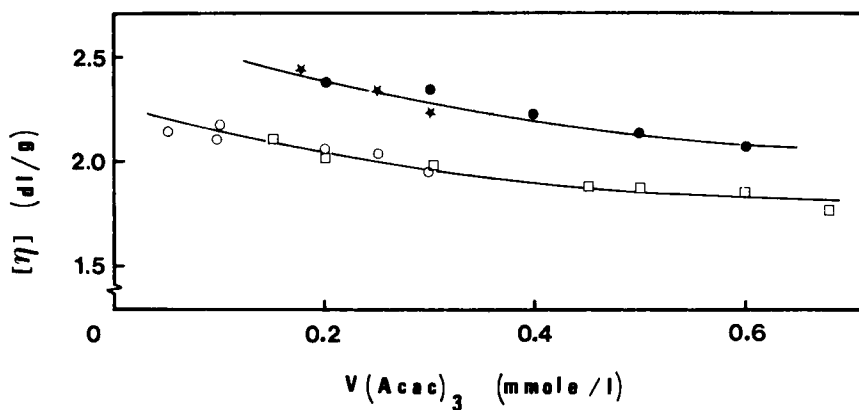P/Al = 0.05.

FIG. 13. Dependence of quaterpolymer intrinsic viscosity on the type
of Lewis base added to catalyst and on the catalyst concentration. Con-
ditions as in Fig. 12; (○) = no base, (□) = $P(n-C_4H_9)_3$, (★) = C_5H_5N, and
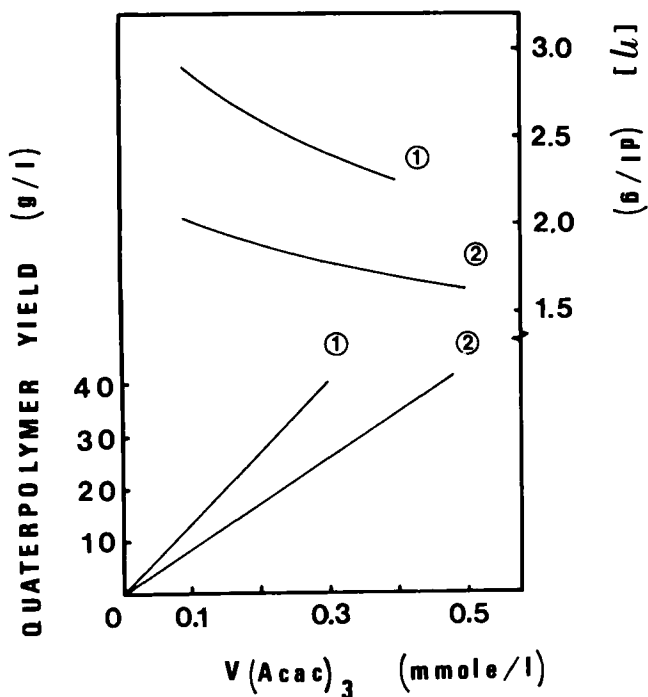(●) = $P(C_6H_5)_3$.

FIG. 14. Quaterpolymer based on II and III: dependence of the yield and $[\eta]$ on catalyst concentration. Conditions as in Fig. 1, except: II = 34.6 mmoles/liter; III = 9.0 mmoles/liter; (1) = -10°C, and (2) = 0°C.

presence of acidic adventitious impurities or intrinsic acidic catalyst systems is avoided.

The reciprocal influence of two polyenes participating in a quaterpolymerization reaction appear to depend mainly on the specific coordinating abilities to catalyst centers of single comonomers which, however, compete reciprocally and exclude one another other from the propagation reaction. Therefore, the ability of every polyene to interfere with the active species and other partners of the reaction, depends on its electron donor efficiency and on the intrinsic reactivity of the double bond that is subjected to opening; both these aspects determine the
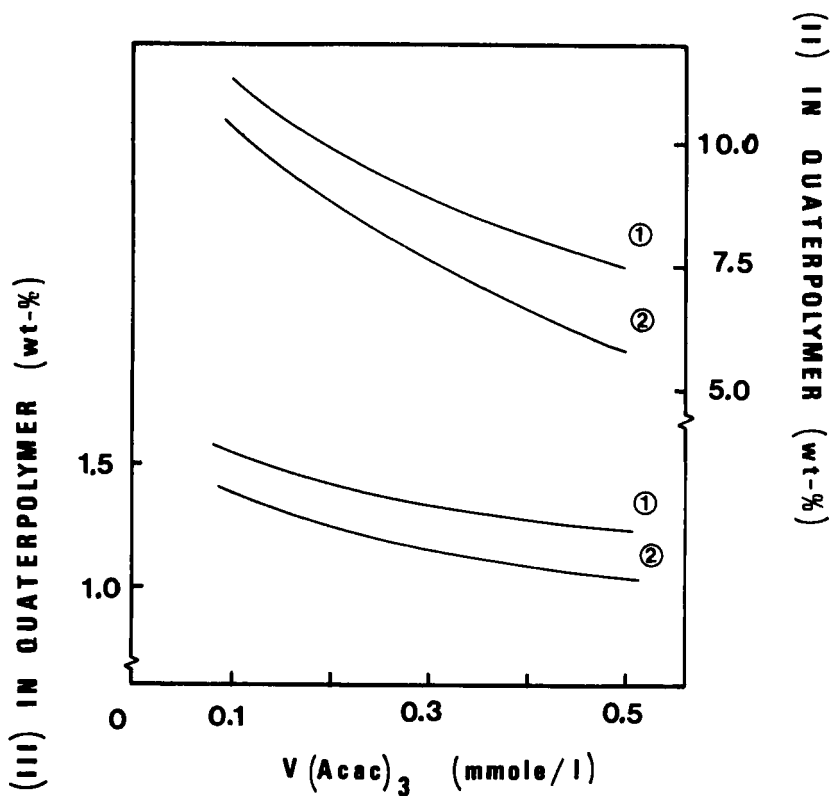
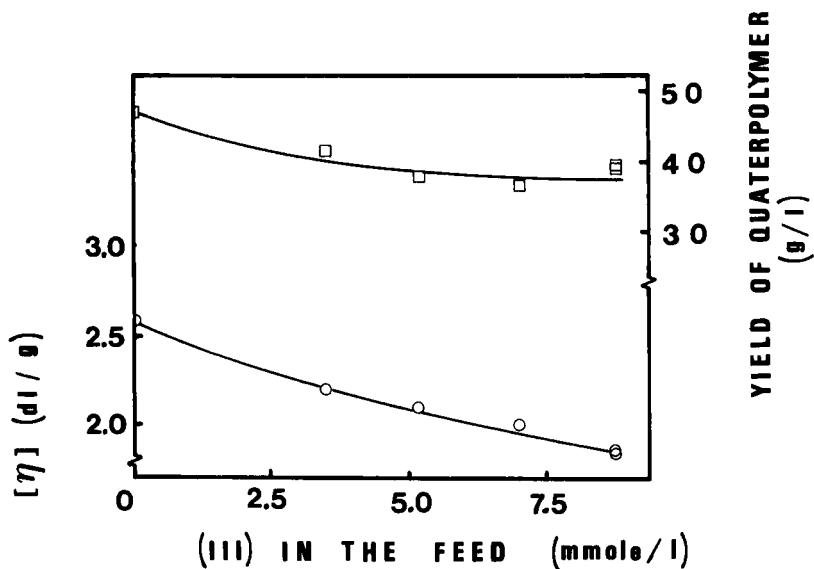FIG. 15. Content of II and III in quaterpolymer of Fig. 14.

FIG. 16. Influence of the concentration of III on the quaterpolymer yield and on $[\eta]$; II = 34.6 mmoles/liter; VAcac$_3$ = 0.5 mmole/liter; T = 0°C.
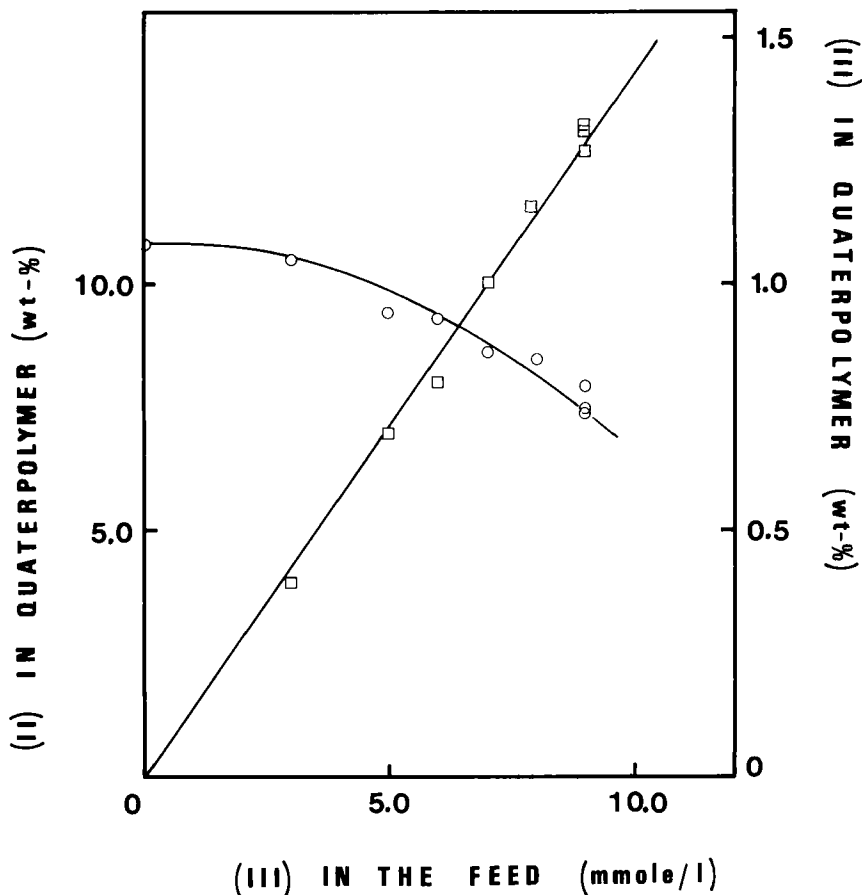
FIG. 17. Influence of the concentration of III on the content of polyenes in quaterpolymer. Conditions as in Fig. 16.

actual concentration of polyene in the polymer. On the other hand, the influence of Lewis bases appears to be a more complex phenomenon than the competition between two polyenes participating in the quater-polymerization process. In fact, for low values of the base/catalyst molar ratio an increase of the polymer yield is sometimes observed, whereas for relatively higher values of the same ratio a significant decrease of the overall polymerization rate is generally evident.

TABLE 1. Fractionation of a Sample of Quaterpolymer Containing I and III

Fraction	$[\eta]^a$ (dl/g)	I (wt%)	III (wt%)	C_2H_4 (wt%)
1	3.21	5.6	0.96	62
2	2.87	5.1	0.95	63
3	2.49	5.4	0.89	n.d.
4	2.10	4.7	0.89	60
5	1.80	4.9	1.00	n.d.
6	1.16	5.6	1.03	60
7	0.90	5.7	0.92	60
8	0.54	4.3	0.85	n.d.
9	0.53	n.d.	0.73	n.d.
Initial sample	1.89	6.1	1.07	60

^{a}From toluene at 30°C.
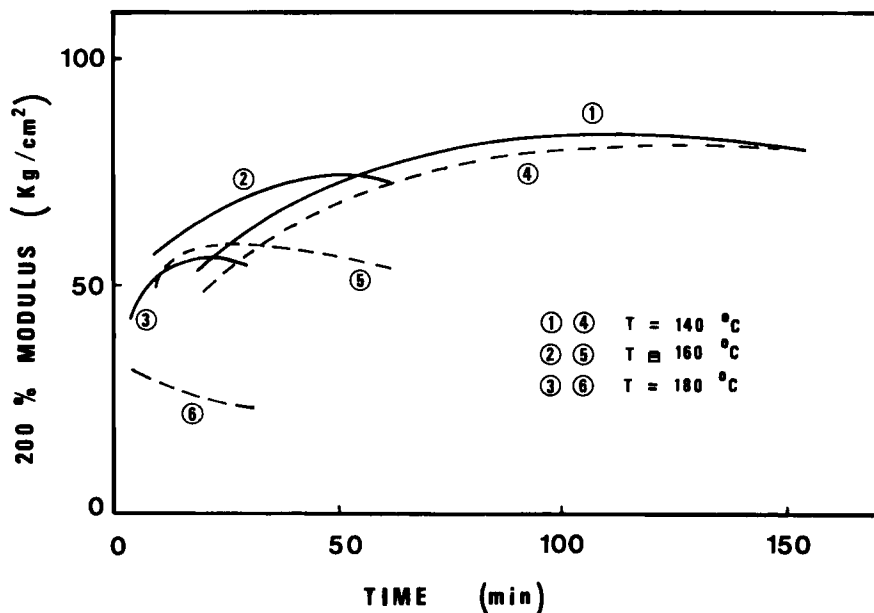
FIG. 18. Covulcanization kinetics at different temperatures of blends of quaterpolymer containing I-III (10 and 0.96 wt%, respectively) and 1,4-cis-polyisoprene (IR). Reference (broken lines) to 5-ethylidene-2-norbornene based EPDM (10 wt% of ENB) blends. Recipes: Quaterpolymer (or EPDM) = 75; IR = 25; HAF = 80; Circosol-4240 = 40; ZnO = 5; S = 2.1; AO-2246 = 1; stearic acid = 1; Vulkacit = 1.6 (at 140°C), 1.2 (at 160°C), and 0.8 (at 180°C).

TABLE 2. Spectroscopic Properties of Quaterpolymers Containing I, II, and III

Sample	IR absorptions (cm^{-1})	UV absorption ($m\mu$)
A[a]	3035 ($\nu_{=CH}$); 1607 ($\nu_{C=C}$); 942 (Ref. 29); 690 ($\gamma_{=CH}$)	254
B[b]	3035 ($\nu_{=CH}$); 1610 ($\nu_{C=C}$); 942 (Ref. 29); 883 (Ref. 10); 735 (sh; [10]); 690 ($\gamma_{=CH}$)	254

[a]Containing 5.9 and 1.2 wt%, respectively, of I and III.
[b]Containing 8.0 and 1.2 wt%, respectively, of II and III.

TABLE 3. Solution Properties of Ethylene-Propylene Based Ter- and Quaterpolymers Containing I, II, and III[a]

Sample	C_2H_4 (wt%)	I (wt%)	II (wt%)	III (wt%)	$[\eta]$[b] (dl/g)	$\overline{M}_v \times 10^{-3}$ [c]	$\overline{M}_n \times 10^{-3}$	$\overline{M}_v/\overline{M}_n$
1	61	4.8	-	-	2.72	301	97.8	3.08
2	59	-	7.0	-	3.34	399	123	3.24
3	59	-	-	1.2	1.94	187	73.5	2.54
4	60	5.9	-	1.2	1.83	174	82.2	2.11
5	61	-	8.0	1.2	2.14	214	88.1	2.43

[a]Prepared at 0°C in toluene under the same conditions with the system $VAcac_3$-Et_2AlCl.
[b]From toluene at 30°C.
[c]From the relationship $[\eta] = 3.1 \times 10^{-4}\ \overline{M}_v^{0.72}$ [12].
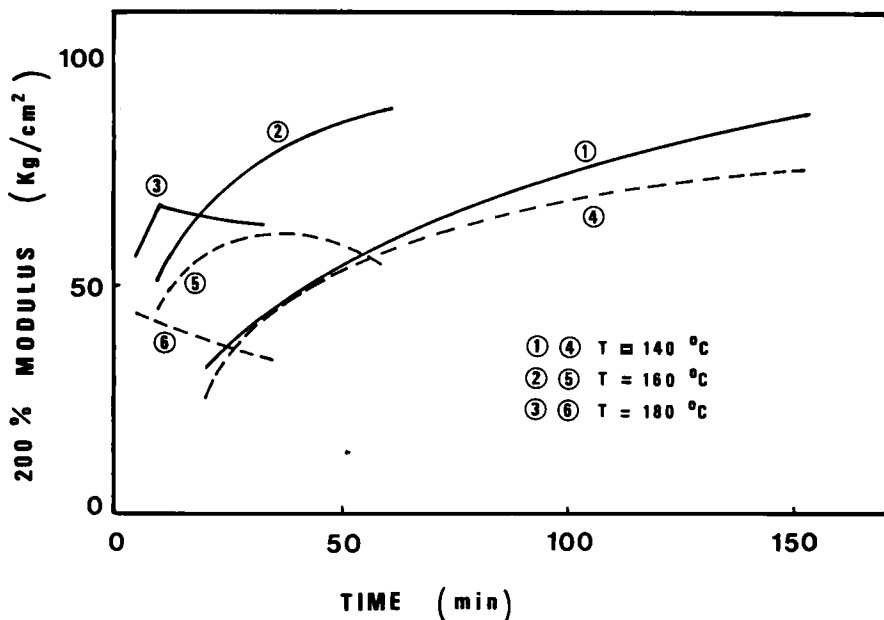
FIG. 19. Covulcanization kinetics at different temperatures of blends of quaterpolymer containing I-III (10 and 0.96 wt%, respectively,) and IR. Reference (broken lines) to ENB-EPDM (10 wt% of ENB) blends. Recipes: Quaterpolymer (or EPDM) = 75, IR = 25, HAF = 80, Circosol-4240 = 40, ZnO = 5.9, S = 2.97, AO - 2246 = 1, stearic acid = 2, Vulkacit = 0.95, and Retarder W = 0.24.

Also, the coordination ability and the basic strength of the electron donor molecules strongly influence ter- and quaterpolymerization kinetics involving Triene III. Furthermore, donors containing aromatic rings, e.g. C_5H_5N or $P(C_6H_5)_3$, significantly increase the MW of quaterpolymer containing I and III.

On the basis of data now available, it is impossible to give a satisfactory explanation of the different results which seem to reflect a significant modification of an unknown number of individual steps in the entire quaterpolymerization process.

The above results confirm that a system of conjugated double bonds, as it is present in III, imparts to the triene a poisoning efficiency of the catalyst sites which is about fivefold higher than in Diene I. However, the high reactivity of the substituted cyclopentadienyl ring introduced by III, which allows excellent behavior during the covulcanization processes of these elastomers with highly unsaturated rubbers, is still present in quaterpolymers which have levels of III close to 1 wt%.
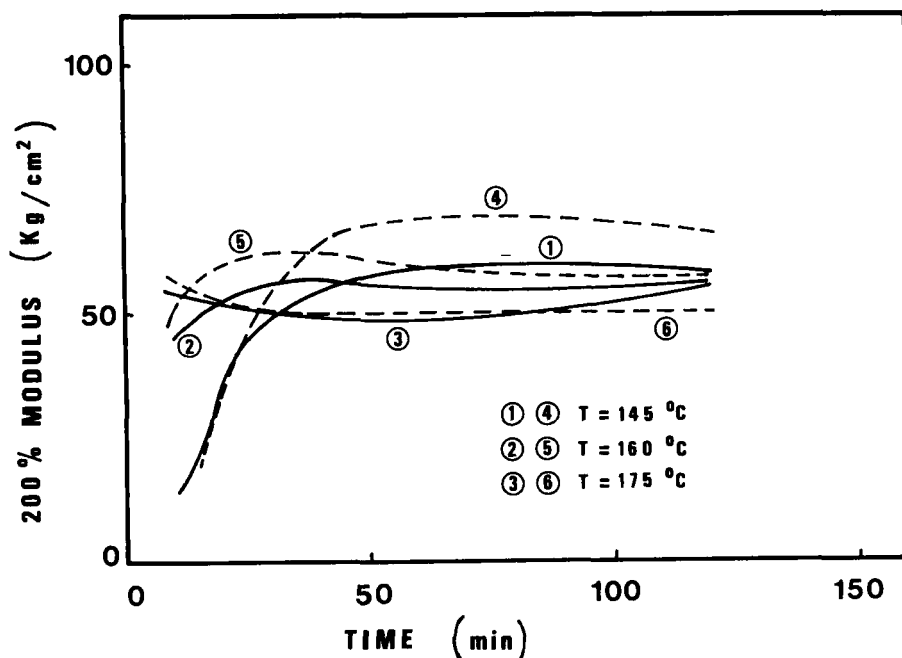
FIG. 20. Covulcanization kinetics at different temperatures of blends of quaterpolymer containing I-III (3.4 and 0.70 wt%, respectively) and IR. Reference (broken lines) to ENB-EPDM (10 wt% of ENB) blends. Recipes: Quaterpolymer (or EPDM) = 65, IR = 35, FEF = 45, Circosol-4240 = 18, S = 2.5, stearic acid = 1.7, ZnO = 5, BLE = 1.5, Vulkacit = 0.8, and Retarder W = 0.2.

ACKNOWLEDGMENT

REFERENCES

[1] J. Sauer, Angew. Chem., Int. Ed., 6, 18 (1967).
[2] E. K. Gladding, B. S. Fischer, and J. W. Collette, Ind. Eng. Chem., Prod. Res. Develop., 1, 65 (1962).
[3] R. German, R. Hank, and G. Vaughan, Kaut. Gummi, Kunstst., 19, 67 (1966).

[4]   R. E. Cunnigham, J. Polym. Sci., A, 3, 3157 (1965); 4, 1203
      (1966); 5, 243, 251 (1967).
[5]   G. Sartori, A. Valvassori, and S. Faina, Rubber Chem. Technol.,
      38, 620 (1964).
[6]   W. Cooper, D. E. Eaves, M. E. Tunnicliffe, and G. Vaughan,
      Eur. Polym. J., 1, 121 (1965).
[7]   R. J. De Kock and A. Veermans, Makromol. Chem., 95, 179
      (1966).
[8]   E. R. Dolinskaya, L. M. Korobova, I. Y. Poddubnyi, I. A.
      Livshits, and V. N. Sokolov, Vysokomol. Soedin., A-11, 1349
      (1969).
[9]   E. K. Easterbrook, T. J. Brett, F. C. Loveless, and D. N.
      Matthews, 23rd IUPAC Congress, Macromol. Preprint, 2, 712
      (1971).
[10] S. Cesca, G. Bertolini, G. Santi, and A. Roggero, J. Macromol.
      Sci.—Chem., A7, 475 (1973).
[11] S. Cesca, P. V. Curanti, A. Roggero, G. Santi, and M. Bruzzone,
      J. Polym. Sci., Chem. Ed., in press.
[12] S. Cesca, J. Polym. Sci., D, in press.
[13] H. Blümel, Kaut. Gummi, Kunstst., 21, 547 (1968).
[14] I. Solf and H. Herrmann, Plaste Kaut., 18, 243 (1971).
[15] S. Cesca, G. Bertolini, G. Santi, and P. V. Duranti, J. Polym.
      Sci., A-1, 9, 1575 (1971).
[16] S. Cesca, S. Arrighetti, and W. Marconi, Chim. Ind. (Milan),
      50, 171 (1968).
[17] S. Cesca, A. Roggero, G. Bertolini, and W. Marconi, Ibid.,
      (Milan), 50, 183 (1968).
[18] S. Cesca, A. Priola, and G. Santi, J. Polym. Sci., B, 8, 573
      (1970).
[19] S. Cesca, M. L. Santostasi, W. Marconi and N. Palladino,
      Ann. Chim. (Rome), 55, 704 (1965).
[20] S. Cesca, A. Roggero, T. Salvatori, A. De Chirico, and G. Santi,
      Makromol. Chem., 133, 161 (1970).
[21] M. E. Tunnicliffe, D. A. Mackillop, and R. Hank, Eur. Polym. J.,
      1, 259 (1965).
[22] G. Natta, G. Mazzanti, A. Valvassori, G. Sartori, and D. Fiumani,
      J. Polym. Sci., 51, 411 (1961).
[23] J. Boor, Macromol. Rev., 2, 115 (1969).
[24] A. Zambelli, J. Di Pietro, and G. Gatti, J. Polym. Sci., A, 1, 403
      (1963).
[25] G. Ghetti, G. Corradini, V. Bulla, and M. Bruzzone, Chim. Ind.
      (Milan), 51, 1361 (1969).
[26] P. VonSchleyer, J. Amer. Chem. Soc., 89, 699 (1967).
[27] D. J. Pasto and J. A. Gontarz, Ibid., 93, 6909 (1971).
[28] D. L. Christman and G. I. Keim, Macromolecules, 1, 358 (1968).
[29] G. Dall'Asta, G. Motroni, R. Manetti, and C. Tosi, Makromol.
      Chem., 130, 153 (1969).