without consideration of the degree of branching, reproduces qualitatively the frequency dependence of $J'$ observed in Figure 2 at higher frequencies. Here it is assumed that an entanglement from which the shortest radiating strand is $m$ monomer units long will contribute to the effective network only at frequencies exceeding a critical value $\omega(m)$. The function $\omega(m)$ can be determined from the frequency dependence of $J'$ for one sample (A-2) and the other $J'$ curves can be predicted from it, but the calculation is restricted to $m \ll P$. The results are in qualitative agreement in the range of log $\omega$ = 0–4, and in particular they predict the decrease in the secondary loss maximum and its shift to higher frequencies with increased cross-linking and the crossing of the $J'$ curves at higher frequencies. The latter effect is seen to be caused by the increased scission accompanying increased cross-linking, which introduces a larger number of *short* dangling ends in sample A-4. Further details are given elsewhere.[10]

Comparison of the data for A-1 and A-1-E shows that the sol fraction in the former affects the time scale of the relaxation processes in the gel fraction. Thus, at log $\omega = -5.5$, log $G'$ for A-1-E is 5.08. The gel fraction is 0.435 so its contribution to the original sample A-1 should give log $G' = 4.72$. But log $G'$ is actually only 4.23, so the presence of the sol must shift the dispersion to higher frequencies. A more detailed analysis is not attempted at the present time.

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# Reactivities of Nonconjugated Dienes Used in Preparation of Terpolymers in Homogeneous Systems[1]

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ABSTRACT: Twenty-three nonconjugated dienes have been used as the termonomer in polymerizations with ethylene and propylene using vanadium–aluminum alkyl catalysts. Of these dienes, 15 were derivatives of norbornene and 6 were open-chain dienes; tetrahydroindene and a methyl-substituted tetrahydroindene complete the list. All appeared to react as ideal monomers with respect to the copolymerization equation; the values of their reactivity ratio, $r$, with respect to propylene have been determined. The norbornene derivatives are approximately an order of magnitude more reactive than propylene with vanadium catalysts; the other dienes had $r$ values ranging from 0.65 to 1.4, *i.e.*, similar to that of propylene.

The use of Ziegler-type catalysts to prepare high molecular weight polymers from $\alpha$ olefins at moderate temperatures and pressures has been the subject of many articles in the recent literature. A popular class of such polymers has been the amorphous copolymers, particularly those from ethylene and propylene. The simplicity of their preparation, the inherent low cost of the monomers, and the large growing potential market for these elastomers have created this popularity. The compounding and vulcanization of these elastomers and the properties of the vulcanizates have been investigated by Amberg and Brown.[2]

Lukach and Spurlin[3] have reviewed the requirements for forming random copolymers from ethylene and propylene. Adamek,[4] Gresham,[5] and German[6] have described the preparation of similar sulfur-vulcanizable polymers using various dienes to introduce the required unsaturation.

In this paper we present a workable procedure for determining the relative reactivities of several types of dienes, with respect to propylene as well as a procedure for preparing a completely amorphous, random terpolymer of ethylene, propylene, and a diene in a reproducible manner.

Several requirements must be met in order to prepare truly amorphous, uniform copolymers. The first requirement, a soluble catalyst, is satisfied by using various vanadium compounds such as $VOCl_3$, $VCl_4$, $VO(OR)_3$, etc., plus an aluminum alkyl ($R_3Al$, $R_2AlCl$, $R_3Al_2Cl_3$, etc.) mixed *in situ* to form the active species. Rigid control of monomer concentration at the catalyst site is a second important requirement. To accomplish this, pressure, temperature, agitation, monomer feed, and catalyst feed must be controlled within narrow limits. This also includes the maintenance of the proper ratio of aluminum to vanadium so that only the desired catalyst species is formed throughout the polymerization. If such control is maintained, copolymers of a specific composition, molecular weight, and molecular weight distribution can be made.

Implicit in this control is a knowledge of the relative reactivities of the various monomers toward the par-

(1) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1–5, 1968.
(2) L. Amberg and B. F. Brown, *Rubber World*, **147**, (6) 52 (1963).
(3) C. A. Lukach and H. M. Spurlin, *High Polym.*, **18**, 115 (1964).
(4) S. Adamek, E. A. Dudley, and R. T. Woodhams, U. S. Patent 3,211,709 (Oct 12, 1965).
(5) W. F. Gresham and M. Hunt, U. S. Patent 2,933,480 (April 19, 1960).
(6) R. German, R. Hank, and G. Vaughan, *Kaut. Gummi Kunstst.*, **19**, (2) 67 (1966).

ticular catalyst used. Several articles have appeared in the literature listing the values of the reactivity ratio, $r$, when only ethylene and propylene are the monomers involved.[3,7] Such $r$ values for dienes have not been given when dienes are involved in the preparation of terpolymers. Instead, qualitative descriptions have been given to compare the reactivities of termonomers.[6,8,9] In our laboratories we have determined the values of $r$ for 23 dienes under conditions such that the variables were rigidly controlled. This paper is concerned with these determinations.

### Control of Polymer Composition

When two monomers are copolymerized, the instantaneous composition of the copolymers being formed is usually given by copolymerization eq 1,[10] where $M_2$

$$\frac{m_2}{m_3} = \frac{M_2}{M_3}\left(\frac{r_2M_2 + M_3}{r_3M_3 + M_2}\right) \quad (1)$$

and $M_3$ are the mole fractions of the two monomers in the solution, and $m_2$ and $m_3$ are the mole fractions in the copolymer. If the monomers behave ideally, *i.e.*, $r_2r_3 = 1$, then eq 1 reduces to eq 2. Such ideal co-

$$\frac{m_2}{m_3} = r_2\frac{M_2}{M_3} \quad (2)$$

polymerization occurs when the rate of addition of a monomer to a growing chain is unaffected by the nature of the unit last incorporated.

Ethylene and propylene appear to act ideally with the soluble vanadium catalysts over the range of compositions studied. This ideal behavior has already been reported by Lukach and Spurlin[3] for the combination of $(C_2H_5)_2AlCl$ and pentavalent vanadium esters $VO(OR)_3$ in chlorobenzene. Experimental data are presented by them. Using the same procedure, we found the same behavior when a hydrocarbon solvent was used, when $VOCl_3$ was substituted for the vanadate ester, or when the sesquichloride replaced the $(C_2H_5)_2$-AlCl. Theoretically, there are several methods by which the monomer concentration can be kept constant. One method involves the passage of the gases through the reaction medium at a very high rate so that the amount polymerized represents only a small percentage of the gas stream. A more practical method involves a closed reactor held at constant pressure and temperature by the addition of ethylene and propylene at the same rate as they are consumed in the reactor. This requires that all five terms in eq 2 be known. The ratio $m_2/m_3$ is determined by choice. The ratio $M_2/M_3$ can change very rapidly because of the high reactivity and low solubility of ethylene. To maintain a constant ratio it is therefore necessary to be able to determine this ratio quickly so that proper corrective measures can be taken. There is no rapid method available, however, which provides a quantitative measurement of reactive gases dissolved in a solvent containing live catalyst. It is possible to determine the relationship between the composition of the dissolved gases and that of the gases in the head space in a nonflooded reactor assuming equilibrium conditions. Analysis of the gaseous phase can be done quickly by gas chromatography, thus yielding values for $M_2/M_3$. The ethylene/propylene ratio in the gas fed into the reactor can be adjusted to keep the $M_2/M_3$ ratio constant. Thus the value for $r$ can be determined with respect to gas phase composition. Knowledge of the solubility of the gases at various partial pressures makes it possible to calculate the reactivity ratio based on monomer concentration in solution.

When a third monomer is added, a relationship similar in principle to eq 1 is involved. As our study was confined to the region below 5 mol % diene in the polymer, the amount of reaction of diene monomer with diene-terminated growing chain is negligible. We are thus concerned only with addition of diene to a growing chain containing ethylene or propylene end groups. The ratio of ethylene to propylene in the polymers was not varied over a wide enough range to detect a difference of diene reactivity due to the nature of the growing chain end. It was found by experiment that the relative reactivity of propylene to ethylene was not influenced by the presence of the third monomer. Thus it is possible to characterize the relative reactivity of the diene by a single constant, $r_c$, with reference to either ethylene or propylene. Alternatively, eq 2 could be written as

$$\frac{dm_c/dt}{dm_3/dt} = r_c\frac{M_c}{M_3} \quad (3)$$

That is, the rates of addition of the monomers are substituted for the mole fractions in the polymer. Diene reactivities are referred to propylene in all instances in this paper. $M_c$ is the concentration of diene in solution required throughout the polymerization to ensure a constant level of incorporation of the diene into the polymer. The rate at which the diene must be added to the reaction mixture to maintain $M_c$ is expressed as $dm_c/dt$.

Equation 3 takes a form indistinguishable from the ideal copolymerization equation since we operated at very low concentrations of termonomer (<1 mol % for the substituted norbornenes).

A value for $r_c$ for a new monomer was assumed, usually the same $r_c$ already determined for a compound of similar structure, and a run was made on the basis of this assumption. Samples of the reaction solution were removed periodically, and the concentration of unreacted diene was measured. If the assumed value for $r_c$ were incorrect, the concentration of monomer would change with time until an equilibrium concentration resulted. A true value for $r_c$ could be determined from this concentration and from the rate of consumption of propylene. The conditions necessary for the preparation of a uniform terpolymer, which could be analyzed to ensure that the disappearing diene was incorporated uniformly into the polymer, could then be calculated. The procedure was as follows.

First, it was decided what composition with respect

(7) (a) G. Bier, *Angew. Chem.*, **73**, 186 (1961); (b) G. Natta, G. Sartori, A. Valvassori, and G. Crespi, *Hydrocarbon Process., Petrol. Refiner*, **41**, (8), 103 (1962).

(8) E. K. Gladding, B. S. Fisher, and J. W. Collette, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 65 (1962).

(9) G. Natta, G. Crespi, A. Valvassori, G. Sartori, N. Cameli, and V. Turka, *Rubber Plastics Age*, **87**, 459 (1965).

(10) (a) T. Alfrey, Jr., J. J. Bohrer, and H. F. Mark, *High Polym.*, **8**, 8 (1952); (b) G. E. Ham, *Encycl. Polym. Sci. Technol.*, **4**, 165 (1967).

TABLE I

POLYMER CONTROL EXAMPLES[a]

| Variable | Example A | Example B |
|---|---|---|
| Catalyst | $VO(O\text{-}t\text{-}Bu)_3$–$Et_3Al_2Cl_3$ | $VOCl_3$–$Et_3Al_2Cl_3$ |
| Termonomer | DCP[b] | MBN |
| Temp, °C | 40 | 30 |
| Time, min | 51 | 45 |
| Rate of addition of gases | 1 l.[c]/min | 1 l.[c]/min |
| Mole % propylene in gas feed | 40 | 40 |
| Rate of addn of propylene $dm_3/dt$[d] | 16.35 mmol/min | 16.35 mmol/min |
| Rate of addn of termonomer, $dm_c/dt$ | 0.641 mmol/min | 0.232 mmol/min |
| Alkyl, mmol added initially | 2.0 | 2.0 |
| mmol/min during run | 0.361 | 0.391 |
| Total mmol | 20.4 | 19.6 |
| V, mmol/min | 0.019–0.027[e] | 0.019 |
| V, total mmol | 1.20 | 0.83 |
| Al/V (final) | 17.0 | 23.6 |
| Mole % propylene in head space[f,g] | 79, 78, 78, 78 | 80, 79, 79, 78 |
| Propylene in soln, m$M$ | 1295 | 1710 |
| Termonomer, g/l.[g,h] | 0.87, 0.82, 0.85 | 0.40, 0.36, 0.36, 0.36, 0.37 |
| $M_c$, based on last sample, m$M$ | 6.45 | 2.28 |
| Anal. wt % propylene in polymer[g,i] | 42.1, 44.3, 42.8 | 44.9, 46.0, 45.7, 45.8 |
| Unsat. in final polymer in CH=CH/-1000$CH_2$ | 7.9[i] | 2.4[j] |
| RSV[k] | 2.3 | 4.5 |
| Polymer weight, g | 72.7 | 69.2 |
| Yield, g/mmol of V | 58.2 | 83.4 |
| $r_c$[l] | 7.9 | 10.6 |

[a] Two liters of Esso heptane used as solvent. [b] *endo* isomer. [c] As measured at 25° and 1 atm. [d] 400 cc of propylene/min. [e] Variable rate of addition; increased with time. [f] By gas chromatography. [g] Samples removed every 7–10 min. [h] By glpc. [i] By infrared. [j] By titration with ICl. [k] 0.1% in decalin at 135°. [l] From eq 3.

to ethylene, propylene, and diene was desired in the terpolymer. Then the rate at which gas was to be admitted to the reactor during polymerization was chosen. Thus $dm_2/dt$, $dm_3/dt$, and $dm_c/dt$ were set. From eq 2 and 3, the ratios $M_2/M_3$ and $M_c/M_3$ were calculated from the known $r_2$ and $r_c$. The solvent was saturated with a mixture of ethylene and propylene which corresponded to $M_2/M_3$, and since $M_3$ had been measured experimentally, $M_c$ could be calculated. This then determines the amount of diene to be added initially. The catalyst feed rate was then adjusted to maintain $dm_3/dt$ at the chosen rate.

If eq 2 and 3 correctly describe the relationship of the monomers, if the analytical methods are accurate, and if the monomers and catalyst components are kept at constant concentrations, then uniform terpolymers must result. That such would appear to be the case is illustrated by the two examples shown in Table I.

A series of nine polymerizations was run involving *endo*-DCP. Two catalytic systems, namely, $VOCl_3$ or $VO(OtBu)_3$ plus $Et_3Al_2Cl_3$, three solvents (*n*-pentane, *n*-hexane, and Esso heptane), and a temperature range of 30–51° were used. The concentration and rates of addition of both the DCP and propylene were varied. In this series, the calculated value of $r_c$ ranged from 7.1 to 7.9 through a 2.4 variance in the ratio $M_c/M_3$.

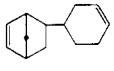
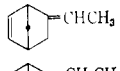
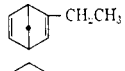
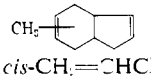
To check reproducibility, example A in Table I was repeated twice more with the following results: final mol % $C_3$ in head space, 78, 78; concentration of DCP in solution, 0.88 and 0.83 m$M$; weight per cent propylene in polymer, 43 and 45%; RSV (reduced specific viscosity, 0.1% in decalin at 135°) 2.2 and 2.2; $r_c$ (calcd), 7.65 and 8.05.

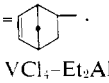
### Discussion of Reactivities

Ideally, a diene to be used in the preparation of a sulfur-vulcanizable elastomer should have two double bonds of widely different reactivity. One should react very readily with Ziegler-type catalysts to ensure ready incorporation into the polymer; the second should be inert during the polymerization but reactive toward the vulcanizing agent. These are the chemical requirements, but economic requirements as well would enter into the choice of a termonomer for the preparation of a commercial elastomer. Many types of dienes have been tested for this use and are reported in the literature.[8,9] Conjugated dienes, even those with one sterically hindered double bond which effectively prevents its use in polymer formation, are poor choices. They evidently complex with the catalyst, changing the course of polymerization with ethylene and propylene. This changes the nature of the polymers and also cuts yield drastically. Unconjugated dienes behave much more satisfactorily, whether they be open chain or cyclic. This study involved a number of both types of dienes, and the following observation regarding them were made.

Four catalyst systems were employed: $VOCl_3$–$Et_3Al_2Cl_3$; $VO(O\text{-}t\text{-}Bu)_3$–$Et_3Al_2Cl_3$; $VCl_4$–$(i\text{-}Bu)_3Al$; and $VCl_4$–$Et_2AlCl$. As can be noted in Table II, the values of the reactivity ratios obtained with these various catalysts varied from each other no more than did replicate determinations based on a single catalyst. The reactivity of the dienes toward these catalysts ap-

TABLE II
VALUES OF REACTIVITY RATIO FOR VARIOUS DIENES

| Compound[a] | Name | Abbreviation | Reactivity ratio, $r$[b] A[c] | B[c] | C[c] | D[c] |
|---|---|---|---|---|---|---|
|  | *endo*-Dicyclopentadiene | *endo*-DCP | 7.6 | 7.3 | | |
|  | *exo*-Dicyclopentadiene | *exo*-DCP | 14.4 | | | |
|  | 1,2-*endo*-Dihydrodicyclopentadiene | DHDCP | | 6.8[d] | | |
| RH | 2-Norbornene | NB | 16.5[d] | | | |
| $RCH{=}CH_2$ | 5-Vinyl-2-norbornene | VN | 5.8 | 5.1 | | |
| $RCCl{=}CH_2$ | 5-($\alpha$-Chlorovinyl)-2-norbornene | CVN | <2.0 | | | |
| $RC(CH_3){=}CH_2$ | 5-Isopropenyl-2-norbornene | IPN | | 13.6 | | |
| $RCH_2CH_2CH{=}CH_2$ | 5-(3-Butenyl)-2-norbornene | 3-BN | 8.8 | | | |
| $RCH_2CH{=}CHCH_3$ | 5-(*cis*-2-Butenyl)-2-norbornene | cis-2-BN | 7.2 | 7.7 | | |
| $RCH_2(CH_3){=}CHCH_3$ + $RCH_2CH{=}C(CH_3)_2$ | 5-(2- or 3-methyl-2-butenyl)-2-norbornene | MBN[e] | 9.5 | 10.3 | | |
| $RCH(CH_3)CH{=}CHCH_3$ | 5-(1-Methyl-2-butenyl)-2-norbornene | 1-MBN | | 10.1 | | |
|  | 5-(3-Cyclohexenyl)-2-norbornene | CHN | 11.9 | | | |
|  | 5-Methylene-2-norbornene | MN | | 5.6 | 6.6 | |
|  | 5-Ethylidene-2-norbornene | EN | | 16.0 | | |
|  | 2-Ethyl-2,5-norbornadiene | END | | 7.2 | | |
|  | Tetrahydroindene | THI | | 0.9[d] | | |
|  | Methyltetrahydroindene | MTHI | | 0.9[d] | | |
| *cis*-$CH_2{=}CHCH_2CH{=}CHCH_3$ | *cis*-1,4-Hexadiene | *c*-HD | 0.66 | 0.67 | 0.65 | |
| *trans*-$CH_2{=}CHCH_2CH{=}CHCH_3$ | *trans*-1,4-Hexadiene | *t*-HD | | 0.69 | | |
| $CH_2{=}CHCH_2CH_2CH(CH_3)CH{=}C(CH_3)_2$ | 5,7-Dimethyl-1,6-octadiene | 5,7-DMO | 1.1[d] | | | |
| $CH_2{=}CHCH(CH_3)CH_2CH_2CH{=}C(CH_3)_2$ | 3,7-Dimethyl-1,6-octadiene | 3,7-DMO | 0.77[d] | | | |
| $CH_2{=}CH(CH_2)_6CH{=}CH(CH_2)_7CH_3$ | 1,9-Octadecadiene | ODD | | | | 1.4 |
| $CH_2{=}CH(CH_2)_7CH{=}C(CH_3)_2$ | 11-Methyldodecadiene-1,10 | MDDD | | | | 1.4 |

R =  . [b] With respect to propylene. [c] Catalyst: A, $VO(O\text{-}t\text{-}Bu)_3$–$Et_3Al_2Cl_3$; B, $VOCl_3$–$Et_3Al_2Cl_3$; C, $VCl_4$–$(i\text{-}Bu)_3Al$; D, $VCl_4$–$Et_2AlCl$. [d] Single determinations. [e] 2-MBN/3-MBN = 2/1.

peared to fall into two main groups, each of which could be subdivided. These groups were (1) derivatives of norbornene and (2) open-chain dienes and tetrahydroindene. First, the double bond in the strained ring of norbornene derivatives was very active in polymerizations. The values of $r$ (referred to propylene) ranged from 6 to 16 for these compounds. It can be questioned whether the methods used actually would point out a difference between two monomers with $r$ values of 8 and 10; however, they were sufficiently accurate to detect differences in monomers with $r$ values of 8 and 12. Thus there was no difficulty in determining which monomers were the most reactive. It should also be noted that the monomers used were not 100% pure even though each had been carefully fractionated (Table III). The impurities often were isomers of the monomer, but they could conceivably cause serious deviations in the value of $r_c$.

Although there is no clear-cut parallel between the size of the group in the 5 position in the norbornene ring and its reactivity, it appears that the reactivity is enhanced by an increase in the size. Thus, 5-vinyl-2-norbornene (VN) with $r$ = 5.8 is less active than the 5-butenyl derivatives (3-BN and *cis*-2-BN; $r$ = 7.2–8.8), the 5-(methylbutenyl)norbornenes (MBN and 1-MBN; $r$ = 9.5–10.3), and 5-cyclohexenyl-2-norbornene (CHN, $r$ = 11.9). 5-Isopropenyl-2-norbornene (IPN, $r$ = 13.6) does not fit in this series. Likewise 5-($\alpha$-chlorovinyl)-2-norbornene (CVN, $r < 2$) is distinctly different from the other norbornene derivatives. Yields of polymers in which it was used as the termonomer were normal, but the polymer contained very little combined CVN. CVN appears to be less thermally stable than the other norbornenes; on standing at room temperature in air, it undergoes slow decomposition with color development.

5-Ethylidene-2-norbornene (EN) is a very active monomer with an $r$ value of 16. Its isomer, 2-ethyl-2,5-norbornadiene (END), is only half as reactive ($r$ = 7.2), and 5-methylene-2-norbornene (MN) appears to be even less reactive ($r \sim 6$). The reason for this difference in reactivity is not obvious.

Since the substituted norbornenes were prepared from the Diels–Alder reaction of cyclopentadiene and the appropriate dieneophile, it was assumed that the products used were in the *endo* configuration (see ref

TABLE III
DIENES USED IN TERPOLYMERIZATIONS

| Name | Abbreviation | Source[a] | Bp, °C (torr) | $n^{30}$D | Purity, %[b] |
|---|---|---|---|---|---|
| *endo*-Dicyclopentadiene | *endo*-DCP | A | 87 (50) | [c] | 99 |
| *exo*-Dicyclopentadiene | *exo*-DCP | B | | | 97.2 |
| 5-Methylene-2-norbornene | MN | C | 56 (100) | 1.4802 | 99 |
| 5-Ethylidene-2-norbornene | EN[d] | D | 82.8 (100) | 1.4856 | 98 |
| 2-Ethyl-2,5-norbornadiene | END | D | 57.5 (50) | 1.4661 | 83 |
| 5-Vinyl-2-norbornene | VN | D | 96 (100) | 1.4745 | 96.5 |
| 5-Isopropenyl-2-norbornene | IPN | D | 81.8 (50) | 1.4811 | 94 |
| 5-(α-Chlorovinyl)-2-norbornene | CVN | D | 64.8 (100) | 1.5024 | 91 |
| 5-(3-Butenyl)-2-norbornene | 3-BN | D | 64.9 (100) | 1.4730 | |
| 5-(*cis*-2-Butenyl)-2-norbornene | 2-BN | D | 68.5 (10) | 1.4795 | 87 |
| 5-(2-Methyl-2-butenyl)-2-norbornene | MBN | D | 82.3 (10) | 1.4828 | 99[e] |
| 5-(1-Methyl-2-butenyl)-2-norbornene | 1-MBN[f] | D | 74.4 (100) | 1.4746 | 86 |
| | | | 76.1 (100) | 1.4759 | 96 |
| 5-(3-Cyclohexenyl)-2-norbornene | CHN | E | 109 (10) | 1.5080 | |
| *cis*-1,4-Hexadiene | *c*-HD | D | 65.7 (760) | 1.4081 | 95.5 |
| *trans*-1,4-Hexadiene | *t*-HD | F | 65.7 (760) | 1.4109 | 78.8[g] |
| 3,7-Dimethyl-1,6-octadiene | 3,7-DMO | G | 84 (70) | | 89 |
| 5,7-Dimethyl-1,6-octadiene | 5,7-DMO | G | 80 (70) | | 89 |
| 4,7,8,9-Tetrahydroindene | THI | D | 44 (10) | 1.4929 | >98 |
| 5- or 6-methyl-4,7,8,9-tetrahydroindene | MTHI | D | 58 (10) | 1.4882 | >98 |
| Norbornene | NB | H | | [c] | 99.8 |
| 1,2-*endo*-Dihydrodicyclopentadiene | DHDCP | D | 76 (23) | 1.4979[h] | 94.7 |
| 1,9-Octadecadiene | ODD | D | 151–152 (4) | | 99.8 |
| 11-Methyldodecadiene-1,10 | MDDD | D | 94–95 (10) | | 95 |

[a] A, Enjay Chemical Co.; B, Union Carbide Corp., Chemical Division; C, Dow Chemical Co.; D, prepared at Hercules; E, Farbwerke Hoechst; F, Chemische Werke Hüls; G, Glidden Co.; H, Aldrich Chemical Co. [b] By gas chromatography [c] Solid at 30°. [d] Samples obtained from Union Carbide contained two isomers, presumably *cis* and *trans*, in a 75:25 ratio. Both performed satisfactorily with essentially the same reactivity. [e] Actually a 2:1 mixture of 5-(2- and -3-methyl-2-butenyl)-2-norbornene. [f] Two isomers. [g] Sample also contained 18.2% of the *cis* isomer. [h] 20°.

11). This suggests that a bulky group in the 5 position increases the strain in the ring; this strain is then relieved by the reaction of the double bond. If this were the entire story, it would be expected that 5-alkenylnorbornenes in the *exo* configuration would be less reactive. However, the only known *exo* compound used, *exo*-dicyclopentadiene, was nearly twice as reactive as the *endo* isomer.

The second grouping of dienes has reactivities about a power of ten less than the first group. According to eq 3, if $r_{c_1}$ is $0.1r_{c_2}$, then $M_{c_1}$ must be ten times larger than $M_{c_2}$ to obtain the same level of unsaturation in the polymer. That is, the background concentration of the diene must be that much greater. The reactivity of a vinyl group in an open-chain diene appears to be rather constant within a factor of 2; with calculated values of 0.6–1.4 for $r$, their reactivities are within 50% of the reactivity of propylene itself.

Tetrahydroindene (THI) and methyltetrahydroindene (MTHI) ($r$ = 0.9) are roughly of the same activity as propylene. Presumably the incorporation into the polymer is through the five-membered ring since MTHI has a methyl group on the double bond of the six-membered ring. This would be in agreement with the results of Dall'Asta and Mazzanti,[12] who found that cyclopentene is much more reactive than cyclohexene toward a $VCl_4$–$(Hex)_3Al$ catalyst. That the five-membered ring may be involved in polymerizations has also been shown by Gladding,[8] who used 5,6-dideuteriodicyclopentadiene as the third monomer and found nonremovable deuterium in the polymer.

## Experimental Section

The apparatus used in these experiments was a modified Sutherland reactor.[13] In brief, this reactor consisted of a 1-gal Crouse-Hinds hemispherical glass bowl topped with a gasket and stainless steel plate. The bowl was fabricated from 0.5-in. thick, impact-resistant, borosilicate glass. The plate was tapped to provide entries for an air-driven stirrer, an entrance and exit for a 0.25-in. stainless steel coil used for temperature control, a condenser, gas entry port, thermometer well, and a raised threaded port. A self-sealing rubber device was placed over this port with a threaded cap to hold it in place. In addition, a curved piece of 0.25-in. stainless steel tubing reached to the bottom of the bowl and was topped with a valve. This permitted the removal of liquid samples during the polymerizations.

To ensure rapid gas–liquid equilibrium, the stirrer shaft was connected to a hollow shaft by means of two collars liberally drilled with holes. The outside shaft below the bottom collar had a concave conical surface and was fitted with vertical fins. A small plate could be raised or lowered on the inside solid shaft to widen or narrow the slit between it and the bottom of the conical surface. Liquid thrown out at high speed by the fins, above and below the slit, entrapped gas in a manner similar to that of an aspirator. The gas recirculation rate was measured as 30 l./min at 600 rpm.[14] Much higher stirrer speeds were used in actual runs. As the gas consumption was 1 l./min (as measured at atmospheric pressure and 25°) and the polymerization pressure was 3

(11) J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 18 (1967).
(12) G. Dall'Asta and G. Mazzanti, *Makromol. Chem.*, **61**, 178 (1963).
(13) J. D. Sutherland and J. P. McKenzie, *Ind. Eng. Chem.*, **48**, 17 (1956).
(14) Dr. Vincent Verplanck, private communication.

atm, less than 1% of the monomer was consumed per pass. Control of the temperature to ±0.1° was achieved by injecting steam into an air water mixture passing at high velocity through the coil. A low-lag thermistor control was used to actuate the steam-injection solenoid valve.

The general procedure used for terpolymerization was as follows. After addition of 2 l. of Esso heptane (dried over molecular sieves) to the Sutherland reactor, the reactor was evacuated using a water aspirator, and propylene (dried by passage at 50 psig through a column of molecular sieves) was passed into the reactor with stirring until the gas pressure was about 0 psig. The reactor was again evacuated and pressurized with propylene to atmospheric pressure. The temperature was raised to the desired level and more propylene added until the pressure reached a predetermined level. For example, if it were desired that a terpolymer containing ethylene and propylene units in a 7:3 ratio be made at 50°, then the addition of propylene was continued until the pressure reached 17 psig. Then ethylene, also dried in a fashion similar to the propylene, was passed into the reactor with stirring until the pressure reached 30 psig. Analysis of the gas phase by gas chromatography indicated that the gas phase contained ethylene and propylene in a 32:68 ratio. The aluminum alkyl was added in the amount of 2 mmol along with the predetermined amount of termonomer through the self-sealing liner using syringes.

Three liquid streams were then fed continuously to the reactor. The first contained a solution of the aluminum alkyl, the second a solution of the termonomer, and the third a solution of the vanadium compound. The first two were introduced at a constant rate (0.43 ml/min) using a double-barreled stainless steel syringe driver. The concentration of the alkyl was usually from 0.5 to 1.0 *M* and the concentration of the termonomer varied according to its reactivity and the level of incorporation desired. The concentration of the vanadium compound was normally 0.05 *M*, and this solution was fed by means of a positive displacement pump. Polymerization normally began within 2 min, as shown by a slight drop in pressure; immediately the addition of a cubic meter of gas per minute (700 cc of ethylene plus 300 cc of propylene, as measured at 25° and atmospheric pressure) was begun and maintained at a constant rate throughout the reaction. The solution of vanadium compound was added at the rate necessary to maintain the pressure constant at 30 psig. During the course of the polymerization, several samples of gas were removed and analyzed by gas chromatography. Liquid samples were removed likewise through the dip tube, quenched with 2-propanol, and analyzed for termonomer concentration. The polymer was isolated by evaporating the solvent, and the propylene and diene content were measured.

At the end of the polymerization, addition of all catalyst components and gas were stopped. The solution was blown through the dip tube under autogenous pressure into bottles containing several milliliters of 2-propanol plus 10 ml of a 2% solution of 2,2-methylenebis(4-methyl-6-*t*-butyl) sulfide to prevent oxidation. The solution was washed with distilled water until neutral and the polymer recovered as a thin film by drying in glass trays to remove the solvent.

**Reagents.** **Esso heptane** is a hydrocarbon cut with boiling point range 94–99°, containing 52.5% naphthenes, 44.6% paraffins, 2.3% aromatics, and 0.6% internal olefins. **Dienes:** the pertinent data are given in Table III. **Ethylaluminum sesquichloride, diethylaluminum chloride, and triisobutylaluminum** were obtained from Texas Alkyls, Inc. **Vanadium oxychloride and vanadium tetrachloride** were purchased from Anderson Chemical Division, Stauffer Chemical Co., Weston, Mich. ***t*-Butyl orthovanadate** was obtained from the Anderson Chemical Division, Stauffer Chemical Co., as a solution in heptane. **Ethylene** was U. S. Industrial Chemical Co. Product dried by passage through a 5-ft column 1.88 in o.d. of type 4A molecular sieves under 50 psig. **Propylene,** Sinclair Refining Co., was purified in the same manner as ethylene. The solubility of propylene in Esso heptane was measured in our laboratories by Dr. F. E. Williams. For calculation in the determination of the value of $r_c$, the solubility concentration used was 850 mmol/l. at 50° and 17-psig partial pressure of propylene.

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