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Ethylene-Propylene Based Terpolymers Containing Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene

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SUMMARY:

Tricyclo[5.2.1.0^{2.6}]deca-2,5,8-triene (1) (trivial name: dehydro-isodicyclopentadiene) or a mixture of its methyl derivatives were used as termonomers to obtain ethylene-propylenetriene terpolymers (EPTM's) having unusual properties in the curing process, even at low levels of triene (ca. 1 wt-%). Three types of catalyst systems have been investigated, i.e. based on VCl₄, VO[O(CH₂)₃CH₃]₃, or V(acac)₃ and (C₂H₅)₂AlCl. Several parameters of the terpolymerization process were studied (e.g. Al/V mole ratio; catalyst and termonomer concentration; polymerization time; presence of a Lewis base or chain transfer agent) and their influence on \overline{M}_v and EPTM composition were evaluated. Fractionation data and the use of model compounds allow to conclude that 1 enters EPTM chains randomly and by selective opening of the norbornenic double bond, whereas the conjugated diene system is involved in side-reactions if the catalyst has some acid character or the concentration of the triene is above some critical values.

ZUSAMMENFASSUNG:

Tricyclo[5.2.1.0^{2.6}]deca-2,5,8-trien(1)(Trivialname: Dehydro-isodicyclopentadien) oder eine Mischung seiner Methylderivate wurden verwendet als Termonomere zur Herstellung von Äthylen-Propylen-Trien Terpolymeren (EPTM) mit ungewöhnlichen Eigenschaften beim Vulkanisationsprozeß, selbst bei niedrigem Triengehalt (etwa 1 Gew.-%). Drei Arten von Katalysatorsystemen wurden untersucht, und zwar auf der Basis von VCl₄, VO[O(CH₂)₃CH₃]₃ oder V(acac)₃ und (C₂H₅)₂AlCl. Es wurden mehrere Parameter des Terpolymerisationsverfahrens untersucht (z. B. Al/V Molverhältnis; Katalysator und Termonomerkonzentration; Polymerisationsdauer; Anwesenheit einer Lewisbase oder eines Kettenübertragungsmittels) und ihre Wirkung auf \overline{M}_v und die Zusammensetzung von EPTM ausgewertet. Die Fraktionierungsangaben und die Anwendung von Modellverbindungen führen zu dem Schluß, daß 1 in die EPTM-Ketten statistisch und durch selektives Öffnen der norbornenischen Doppelbindung eintritt, während das konjugierte Diensystem Nebenreaktionen eingeht, wenn der Katalysator einen sauren Charakter aufweist oder die Trienkonzentration eine kritische Konzentration übersteigt.

Introduction

Unsaturated ethylene-propylene terpolymers containing a conjugated diene system as pendant group have been described recently¹⁻⁵⁾. The interest for this particular class of synthetic elastomers, whose unsaturations are very reactive in the curing process, is founded on the possibility of co-vulcanizing them with highly unsaturated rubbers, as, for instance, SBR or 1,4-*cis*-polyiso-prene. Such a result can be accomplished when the termonomer content is very low⁶⁾, i.e. ca. 1 wt-% in the case of conjugated dienic systems having an obliged *cisoid* configuration⁷⁾, as it occurs in the cyclopentadiene ring⁴⁾. The peculiar reactivity of this cyclic diene system has been further investigated by employing



tricyclo $[5.2.1.0^{2.6}]$ deca-2,5,8-triene (1) (trivial name: dehydro-isodicyclopentadiene), as termonomer in EPTM^{*}) synthesis. Several variables of the terpolymerization process and the main physico-chemical properties of the resulting terpolymer have been studied and are reported in this paper together with some parameters of the vulcanization process.

Experimental Part

Materials

Tricyclo[5.2.1.0^{2.6}]*deca*-2,5,8-*triene* (1): Triene 1 was prepared by hydroxylation of "*endo*"-dicyclopentadiene (DCP) with SeO₂ in dioxane⁸⁾. The yield of 1-hydroxy-DCP was 52% whereas the successive dehydration on Al₂O₃ at 260°C gave 1; yield: 57%. The crude 1 was crystallized twice from methanol; mp 45°C (lit.⁹): 44°C). Purity: >99,9% according to VPC.

UV (hexane): 235 nm ($\varepsilon = 5300 \ 1 \ mol^{-1} \ cm^{-1}$) (lit.⁹): 235; $\varepsilon = 3706 \ 1 \ mol^{-1} \ cm^{-1}$). NMR (CCl₄): $\delta = 2,1$ (2H¹⁰), 3,2 (2H⁴), 3,4 (H¹ + H⁷), 5,5 (H³ + H⁵), and 6,3 ppm (H⁸ + H⁹).

^{*)} According to the ASTM nomenclature EPTM is the abbreviation which denotes an ethylene-propylene-triene terpolymer^{11a)}.

IR (KBr): 3065, 3110 (v_{C-H}) (lit.⁹): 3090, 3130), 1558, 1598, 1630, 1668 ($v_{C=C}$) (lit.⁹): 1602, 1633, 1642, 1676), 717, 766, 810, 898 cm⁻¹ (γ =CH) (lit.⁹): 717, 765, 813, 900 cm⁻¹).

Tricyclo[5.2.1.0^{2.6}]*deca*-2,5-*diene* (2): A model compound of 1, i.e. its 8,9-dihydroderivative 2, was obtained through preliminar hydrogenation of DCP with the stoichiometric amount of H₂ in the presence of Pd (supported on activated carbon), at room temp. and at atmospheric pressure in ethanol solution⁹⁾. Yield: 95%. The successive steps of hydroxylation and dehydration were performed as described in the case of DCP. Final purity: 96,5% according to VPC, the main impurity being 1,2-dihydro-DCP; bp₁₀ 65°C; n_D^{20} =1,3342; d_{20} =1,0143; MS: m/e 132 (M⁺); UV (hexane): 242 nm (ϵ =36711 mol⁻¹ cm⁻¹) (lit.⁹⁾: ϵ =3606 l mol⁻¹ cm⁻¹ at 243 nm).

5,6-Dimethylene-2-norbornene (3): 3 was prepared¹⁰⁾ by dehydrohalogenation of 5,6-dichloromethyl-2-norbornene, which, in turn, was obtained through Diels-Alder condensation of cyclopentadiene and 1,4-dichloro-2-butene. Yield: 40% (with respect to 5,6-dichloromethyl-2-norbornene). Bp₁₅ 47-48°C. Purity: ca. 95% according to VPC, the main impurity being DCP and an unknown hydrocarbon having M = 118. MS: m/e 118 (M⁺), 117,91, and 66 (cyclopentadiene from retro-Diels Alder fragmentation).

5-(2-Vinyl-3-butenyl)-2-norbornene (4): 4 was obtained by reacting 5-bromomethyl-2-norbornene⁴⁾ with the sodium derivative of 1,4-pentadiene, which, in turn, was prepared from phenylsodium and 1,4-pentadiene¹¹⁾. Final yield: 17% (with respect to 1,4-pentadiene); $bp_{0.1}$ 46°C. MS: m/e 176 and 66.

Methylation of 1: Attempts of methylating 1 were carried out in THF at 80 °C with the potassium derivative of 1, using a stoichiometric amount of CH_3I . An overall conversion of 42% was observed, but a mixture of mono-, di- and trimethyl-derivatives of 1 was obtained. The change of the stoichiometric ratio of the reactants or the modality of contacting them did not modify substantially the composition of the reaction mixture. Attempts to separate the components of the mixture by fractional distillation were unsuccessfull.

It is very likely that the metallation of 1 implies the possibility of successive reactions by the electrophilic attack of the alkyl halide on the substituted cyclopentadienide anion. Consequently, some unsubstituted 1 was present in the reaction mixture, even though alkyl halide was present in excess.

On the other hand, the presence of electron releasing substituents increases the nucleophilicity of cyclopentadienide anion and hence all the hydrogen atoms of the initial cyclopentadiene derivative can be substituted, although the presence of substituents hinders, for steric reasons, the reactivity of substituted cyclopentadienide anion. The same conclusion was reported also by *Rybinskaya* and *Korneva*¹²) when the methylation of cyclopentadiene was considered. Furthermore, according to *Mironov* et al.¹³) thermodynamic equilibria take place between the hydrogen atoms of the alkylcyclopentadiene derivatives, also in the absence of ionic species. The final result is the prevalent distribution of the alkyl substituents of cyclopentadiene ring on the unsaturated carbon atoms of the ring. However, since the attaining of the equilibrium conditions is a relatively slow process the separation of 3-methyl-derivative of 1 can be possible, as we observed in a fraction obtained from the reaction mixture.

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After removal of the solvent and unreacted components, a typical reaction mixture yielded a liquid fraction; bp₂ 45–60°C; $n_D^{20} = 1,5330$; $d_{20} = 0,9719$. The results of VPC and MS are reported in Tab. 1.

Tab. 1. Composition of the central fraction collected from the methylation mixture of 1

Elution time ^{a)}	Product ^{b)}	Percentage ^{c)}
10 min 20 s } 11 min 28 s }	Hydrogenated 1 + me- thyl-derivative of 1	5,4
14 min 25 s	Methyl- + dimethyl-deriv. of 1	23,0
17 min 5 s	Methyl-deriv. of 1+unreacted 1	36,5
20 min 7 s	Mono-, di- and trimethyl-deriv. of 1	35,1

^{a)} Column EAS dimethyl succinate; 5 m; $T_{column} = 145 \,^{\circ}\text{C}$; $T_{evaporator} = 180 \,^{\circ}\text{C}$; carrier: He; flow: 1 cm³ s⁻¹.

^{b)} Determined only through the masses of individual gas-chromatographic signals.

^{c)} By evaluation of the areas of VPC signals.

Tritiated 1: Radioactive 1 was prepared as tritiated product from inactive 1 and T_2O (supplied by the Radiochemical Center, Amersham, England) in the presence of catalyst (Pd 5% on Na₂CO₃). After 24 h at 55°C and 24 h at room temp. the reaction mixture was washed with H_2O , dried on MgSO₄ and radioactive 1, purified by crystallization, was collected into phials by sublimation i. vac.

Details of this preparation will be published in the future.

Other products: Ethylene, propylene, catalyst components, and solvents had the same origin and were subjected to preliminar treatment as previously reported 3.17).

Procedure: The terpolymerization equipment and experimental conditions adopted have been described elsewhere³.

Analyses: The procedure adopted for the spectroscopic analyses of terpolymer in IR and UV regions (respectively, for propylene and termonomer dosage) was reported previously³⁾. The specific molar absorption coefficient of **2** at 242 nm was $\varepsilon = 2245$ l mol⁻¹ cm^{-1*}) and was used to determine the content of triene in EPTM, as in the case of other EPTM's containing different conjugated diene systems^{3,4)}.

The use of chemical methods (e.g. IBr absorption) affords results ca. twice as high as the data of the absolute method^{7,29}.

NMR, MS, VPC and X-ray measurements were carried out applying the same instruments and procedures which have been already described³⁾.

^{*)} This value of ε , different from the above reported one, was calc. by drawing the base-line as a tangent to the spectrum between 214 and 270 nm.

Also radioactivity measurements were carried out with the liquid scintillation method as reported previously³⁾. A detailed discussion of the procedures adopted³⁾ and their critical evalutation will be published elsewhere¹⁵⁾.

Fractionation (precipitation method) and intrinsic viscosity measurements were carried out in the usual way³⁾.

Vulcanization kinetics¹⁶) were performed with an oscillating disc curometer (Zwick instrument, Mod. 4302; oscillating angle: 1,5 grade; frequency: 3 cycles/min).

Results and Discussion

Different catalyst systems based on vanadium are able to yield EPTM containing 1. The use of non acid systems or of catalyst modifiers, belonging to the class of Lewis bases, is generally advisable to minimize side-reactions due to the formation of cationic species which are very efficient towards cyclopentadienylic structures¹⁸.

System $VCl_4/(C_2H_5)_2AlCl/Anisole$

Fig. 1 shows the dependence of terpolymer yield on the termonomer concentration in the feed. While the concentration of 1 in EPTM increases linearly,



Fig. 1. Influence of the concentration of triene 1 on EPTM yield (\Box), terpolymer composition (\blacktriangle , \bullet) and its \overline{M}_v (expressed as $[\eta]^{1,7,29}$) (\odot). Conditions: solvent = toluene; $T = -20^{\circ}$ C; time = 12 min; C₃H₆/C₂H₄=2,5 (gaseous phase); VCl₄=0,25 mmol/l; (C₂H₅)₂AlCl=1,5 mmol/l; anisole=0,75 mmol/l

the catalyst activity is markedly reduced by increasing the termonomer content as occurs, generally, with other trienes containing a conjugated double bond system^{4,19}.

Such a result confirms the poisoning effect of conjugated diene systems which have an enhanced tendency to coordinate to transition metal vacancies with respect to a-olefin monomers and hence, to inactivate catalyst sites. Therefore, it is not surprising that, under the adopted conditions, the utilization of 1 is not high, i.e. in the range 20-50%. While the reactivity of the norbornene double bond of 1 appears to be reduced by the presence of two conjugated double bonds, this dienic system is unreactive in the terpolymerization step (cf. also Sect. on characterization of EPTM based on 1, p. 2554). In fact, according to Fig. 1, the regular increase of the triene content in EPTM occurs as a consequence of increasing levels of 1 introduced in the feed. Such a situation holds, for the catalyst system under investigation, only for low levels of 1 in EPTM, i.e. up to ca. 2 wt- $\frac{1}{2}$, whereas at higher concentration the formation of some gelled material is observed. Therefore, we have preferred to investigate in more details other catalyst systems based, generally, on organic salt of V. Fig. 1 shows also that \overline{M}_{v} of EPTM is apparently independent of the termonomer content, while the C₂H₄ content is increased, with respect to the corresponding EPM, only if 1 in EPTM is higher than 1 wt- $\frac{1}{2}$.

System VO $[O(CH_2)_3CH_3]_3/(C_2H_5)_2AlCl$

Catalysts based on vanadyl alcoholates have been reported to yield EPM and EPDM with high compositional homogeneity^{20,21)}. Indeed, such anticipations have been confirmed also by the synthesis of EPTM based on 1, as it can be seen in Fig. 2 and 3. In Fig. 2 is reported the influence of the catalyst concentration (for different levels of the triene 1) on the average terpolymerization rate and on the C_2H_4 content of EPTM (the corresponding EPM data are also reported).

Fig. 3 shows that the activity of the catalyst system is perturbed in a relatively low extent by the increasing concentration of 1.

According to Fig. 4 a continuous increase of the triene content in EPTM is observed when its concentration in the feed rises; at the same time also a small increase of \overline{M}_{v} occurs. Therefore, some side-reactions of EPTM chains^{7,29} take place if the termonomer concentration in the feed is >10 mmol/l.

Fig. 2. Dependence of average terpolymerization rate on vanadium salt concentration. Conditions: Al/V = 10;solvent = toluene; T=0°C; time=15 min; $C_{3}H_{6}/C_{2}H_{4}=2,5;$ (○): EPM; (□): 1 (7,5 mmol/l); (•): 1 (15,0)mmol/l); (△): 1 (22,5 mmol/l)

 $[VO[O(CH_2)_3CH_3]_3] = 0,63$

1,0

0,5

0

0

mmol/l



Fig. 4. Dependence of 1-content and \overline{M}_{y} of EPTM on the concentration of 1 in the feed. Conditions: as in Fig. 2; [VO[O(CH₂)₃CH₃]₃]=0,25 mmol/l

The existence of chain-transfer reactions due to the aluminum derivative of the catalyst system⁷⁾ is evident from Fig. 5.



Fig. 5. Dependence of \overline{M}_v (expressed as $[\eta]^{1.7.29}$) of EPTM, based on **1**, on the catalyst concentration. Conditions as in Fig. 2

Some conversion time curves of the terpolymerization process in Fig. 6 together with the results of Fig. 7 (EPTM composition and \overline{M}_v at different polymerization times) indicate that the type and number of catalyst centers are not constant during the polymerization time, whereas the average life-time of the growing chains is relatively high under the conditions adopted, as occurs, generally, for many vanadium based catalyst systems used in the EPM synthesis^{7,14,19}.



Fig. 6. Terpolymer yield vs. polymerization time. Condition: solvent = toluene; $T=0^{\circ}C$; $C_{3}H_{6}/C_{2}H_{4}=2,0$; $[VO[O(CH_{2})_{3}CH_{3}]_{3}]=1,0$ mmol/1; $[(C_{2}H_{5})_{2}A|Cl]=10,0$ mmol/1; $(\odot): 1$ (7,5 mmol/1); $(\Box):$ 1 (10,0 mmol/1); (\bullet): 1 (15,0 mmol/1)

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The influence of the mole ratio of the catalyst components is represented in Fig. 8, where it is evident that beyond Al/V = 10 only $\overline{M}_{\rm v}$ is influenced by this parameter, whereas in the range Al/V=3 to 8 a rapid increase of EPTM yield is observed.

Fig. 6



Fig. 8. Influence of the Al/V mole ratio on the average terpolymerization rate, \overline{M}_{v} (expressed as $[n]^{1.7.29}$) and triene content of EPTM. Conditions: Solvent = toluene; $T=0^{\circ}C; C_{3}H_{6}/C_{2}H_{4}=2,5; time=45 min; [VO[O(CH_{2})_{3}CH_{3}]_{3}]=0.9 mmol/l; aniso$ le/Al = 1,0; [1] = 15,0 mmol/l

The presence of a Lewis base as anisole does not modify the type of the conversion time curves of terpolymerization but only the level of the catalytic activity (Fig. 9). Analogously to what has been observed for the catalyst system $VCl_4/(C_2H_5)_2AlCl$ in the case of another EPTM, based on 1-isopropylidene-3a,4,7,7a-tetrahydroindene¹⁴⁾, a maximum of the catalyst activity is observed for the value of the mole ratio anisole/Al=0,15.



Fig. 9. Influence of anisole/Al mole ratio on the terpolymerization yields. Conditions as in Fig. 8; (\bullet): anisole/Al=0,0; (\triangle): 0,15; (\blacktriangle): 0,25; (\Box): 0,50; (\circ): 0,75; (\blacksquare): 1,0

According to Fig. 10–11, different reaction times and different levels of the ternary catalyst do not modify the composition of the resulting EPTM samples, whereas \overline{M}_{v} (expressed as $[\eta]^{1,7,29}$) is increasing for 30 min of polymerization.



Fig. 10. Terpolymer conversion time curves as function of the catalyst concentration. Conditions as in Fig. 8. Al/V = 10; $C_3H_6/C_2H_4 = 2,0$; $[VO[O(CH_2)_3CH_3]_3] = 0,6$ (\blacktriangle), 0,9 (\circ), 1,2 (\Box), 1,8 (\bullet), and 2,4 mmol/l (\triangle)

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Fig. 11. Terpolymer composition and \overline{M}_{ν} (expressed as $[\eta]^{1,7,29}$) vs. polymerization time. Conditions as in Fig. 10

System V(acac)₃/(C₂H₅)₂AlCl

The catalyst system $V(acac)_3/(C_2H_5)_2AlCl$ has been extensively used in the EPTM synthesis^{3,4,19)} and hence, the main features of its behaviour, independently of the particular type of triene used, are known⁷). For instance, also in the case of EPTM based on 1, the optimal values of the mole ratio Al/V have been found to be ≥ 8 , whereas for Al/V < 3.5 no catalytic activity was observed. The triene content of EPTM is independent of the Al/V ratio for values > 10, while \overline{M}_{v} decreases if the Al/V ratio or the catalyst concentration increase. Terpolymerization conversion time curves are progressively depressed by the increase of the triene concentration in the feed, but the shape of the diagrams is substantially unmodified by the inhibiting action of 1. \overline{M}_{v} is always increasing with the polymerization time, independently of the level of catalyst or termonomer. Contrarywise, the content of unsaturation in EPTM is constant at every instant, provided that a continuous supplying of 1 to the feed is guaranted. Such a caution is necessary under the experimental conditions adopted, because of the enhanced reactivity of norbornene double bond, observed also in other dienes²²⁾ or trienes^{3.4)}, having the bicyclo-[2.2.1]hept-2-ene structure.

The overall terpolymerization rate is nearly first order dependent on $V(acac)_3$ concentration.

The content of 1 in EPTM increases linearly when its concentration in the feed rises (Fig. 12), whereas a slight increment of \overline{M}_v is observed at



Fig. 12. Relationship between the concentration of 1 in EPTM and in the feed. Conditions: Solvent=toluene; $T=0^{\circ}$ C; (•): $(C_{2}H_{5})_{2}$ AlCl/V(acac)₃=8; (o): $(C_{2}H_{5})_{2}$ AlCl/V(acac)₃=30; catalyst concentration variable to obtain a constant yield of EPTM (30 g/l); time=30 min

higher levels of **1**. Once again, such a result suggests the existence of side-reactions involving, very likely, the pendant unsaturated groups, which may occur not necessarily during the polymerization step but, for instance, in the finishing $step^{7,23}$.



Fig. 13. Dependence of catalyst activity, \overline{M}_{v} , and content of 1 on the mole ratio Zn/V. Conditions: $[V(acac)_3]=0,15 \text{ mmol/l}; \text{ Al/V}=8,0; [1]=10 \text{ mmol/l}; \text{ solvent=toluene}; \text{temp.=0°C}; \text{time=30 min}; C_3H_6/C_2H_4=2,0$

M of EPTM can be regulated as in the case of $poly(\alpha$ -olefins), i.e. by using chain transfer agents as $Zn(C_2H_5)_2$ or H_2 . The presence of the transfer

agent reduces markedly the overall catalyst activity, both in the case of $Zn(C_2H_5)_2$ (Fig. 13) and H_2 (Fig. 14 and 15), whereas the content of 1 in EPTM is not influenced by them (Fig. 13 and 15).



Fig. 15. Influence of H₂ concentration on EPTM yield, \overline{M}_{v} , and triene concentration. Conditions as in Fig. 13

However, the action of the investigated transfer agents on the spectroscopic properties of EPTM is different. In fact, $Zn(C_2H_5)_2$ apparently reduces only \overline{M}_{ν} , whereas H₂ modifies markedly UV and IR spectra of EPTM. When

the concentration of H_2 is elevated the evaluation by UV becomes impossible, while the content of C_2H_4 rises. The latter result has been observed in EPM prepared under similar conditions (Fig. 16), the increase being ca. 10%, i.e. beyond the error limits of the analytical methods involved (IR and also NMR).



Fig. 16. Influence of H₂ on the C₂H₄ content of EPM and EPTM based on 1; (×), (\triangle) and (\triangle)=EPM; (\circ , \bullet) and (\Box , \blacksquare)=EPTM; (\triangle , \bullet , \blacksquare)=NMR data; (\Box , \circ , \triangle , ×)=IR data; (\Box , \blacksquare , \triangle , \triangle)=runs carried out in the presence 30 l/h of H₂

Therefore, it is evident that H_2 is able to react with the diene system of 1 under the terpolymerization condition adopted; furthermore, it reduces (as $Zn(C_2H_5)_2$ does) the number of catalyst sites and also their type, as is suggested by the change of C_2H_4 content in both EPM and EPTM. Very likely, the hydrogenolytic action of H_2 on the carbon-metal bond of active centers, which originates metal hydride bonds²⁴, changes the active sites in some relevant aspects, probably through a modification of their coordinative ability which may reduce the tendency of propylene to enter ethylene-propylene enchainment. Previous findings, obtained during the studies of the homo-polymerization²⁵ and co-polymerization²⁶ of α -olefins, carried out with coordinate catalysts based on aluminum hydride derivatives, indicate that the resulting systems are less stereospecific and that propylene is less reactive than what is observed with the corresponding systems based on alkyl aluminum derivatives.

EPTM containing methyl derivatives of 1

As it has been discussed in the Exp. Part, we have isolated after methylation of 1 a mixture of mono- (60%), di- (30%) and trimethyl-derivative (10%) of 1. Such a mixture was used in some preliminar experiments reported in Fig. 17, where is evident that it reduces the catalyst activity more than 1 does, probably due to the presence of some impurity which is absent in 1, whereas its utilization and ability to maintain a low \overline{M}_v are enhanced with respect to 1. Also the behaviour in vulcanization experiments of EPTM based on this mixture is very interesting (cf. the section after the next one); therefore, the behaviour of 1 and that of the mixture is quite analogous, respectively, to those of cyclopentadienyl-5-norborn-2-enyl-methane and its methyl-derivative previously described⁴⁾.





Reactivity of 1 towards cationic species

Contrary to organic salts of vanadium, e.g. $V(acac)_3$ or $VO(OR)_3$, which are unable to attack 1, $(C_2H_5)_2AICl$ alone yields an almost quantitative

conversion of 1 to a solid polymer, even in the absence of any co-catalyst (Tab. 2).

A similar result was obtained by Kennedy¹⁸⁾ in the case of cyclopentadiene and other monomers having at least an activated hydrogen atom in allylic position; the catalytic efficiency of $(C_2H_5)_2AlCl$ was attributed to the peculiar mobility of such hydrogen atoms which can be abstracted as hydride ion, while the resulting allylic cation should be the initiating species. However, as is evident in Tab. 2, the polymerization of 1 by cationic catalysts takes place with high yield only if its concentration is 20–50 times higher than that normally used in terpolymerization experiments. More decisive to attain the cationic polymerization of 1 is the electrophilicity of catalysts, as indicated by the experiments of Tab. 2 based on BF₃ $\cdot O(C_2H_5)_2$ or carried out in the presence of a Lewis base (anisole, cf. run 5). In this respect V(acac)₃ also acts as a base towards (C_2H_5)₂AlCl, whereas (CH₃)₃CCl enhances its cationic activity¹⁷).

Other Lewis acids, generally employed as components or Ziegler-Natta catalysts, as TiCl₄, VCl₄ or $C_2H_5AlCl_2$, give high yields of homopolymer of **1**, sometimes as gelled material.

The structure of the soluble portion of 1 homopolymer does not depend on the type of catalyst used and can be ascertained through UV, IR (disappearance of the absorption at 242 nm and appearance of the band at 1553 cm^{-1} , due to the norbornadiene structure), and NMR measurements (the ratio of the areas under the signals due to saturated and unsaturated protons is 4,1 with respect to the expected value of 4,0). All the data agree with the 1,4-opening of the conjugated diene system of 1 and formation of a norbornadiene structure in the repeating unit.

The norbornadiene system has been found reactive towards electrophilic species²⁷) and such a reactivity can be responsible for the formation of insoluble polymer during the cationic polymerization of **1**.

Characterization of EPTM based on 1

X-ray investigations show that EPTM containing 1 is amorphous in the usual range of ethylene contents, i.e. below 75 wt-%, while spectroscopic examinations are able to evidence clearly the presence of 1 in the UV region, namely at 242 nm. The absorption is sufficiently distinct to allow the quantitative evaluation of 1 until the inferior limit of 0,1 wt-% (cf. Exp. Part), whereas IR and NMR spectroscopic methods are unable to give significant absorptions or signals for the low amounts of 1 generally introduced in EPTM.

Run N°	Solvent	$\frac{[1]}{\text{mol } l^{-1}}$	Catalyst Type	Conc. in mmol 1 ⁻¹	T/°C	Time in min	% Yield	$\frac{\left[\eta\right]}{\mathrm{dl}\mathrm{g}^{-1}}$	Notes
-	Toluene	0,50	V(acac) ₃	20	0	60	0		
2	Toluene	0,50	VO[O(CH ₂) ₃ CH ₃] ₃	20	0	09	0	ľ	
ŝ	Toluene	44,0	(C ₂ H ₅) ₂ AlCl	20	0	09	98		20% insoluble
4	Toluene	0,010	(C ₂ H ₅) ₂ AlCl	5,0	0	30	33 ^{b)}		5
			$\int (C_2H_5)_2 AlCl +$	5,07					
5	Toluene	0,010	Anisole +	2,5 >	0	30	0 _{p)}		
			(V(acac) ₃	0,5)					
			((C,Hs),AICI+	5.0)			-		
9	Toluene	0,010	$\{V(acac)_3\}$	1,0 }	0	30	00)	ļ	
7	Toluene	0,50	(C ₂ H ₅)AlCl ₂	5	80	6	100		85% insoluble
8	Toluene	0,50	TiCl ₄	5	- 95	6	86	0,52	
6	CH_2Cl_2	0,50	BF ₃ ·O(C ₂ H ₅) ₂	10	- 80	1020	0	•	
10	CH ₂ Cl ₂	0,56	$\begin{cases} (C_2H_5)_2 A C + (CH_3)_3 C C \end{cases}$	5,0 5,0	- 80	60	96	1	90% insoluble
^{a)} Fro	m toluene at	t 30°C.	^{b)} Determined by VPC ϵ	evalutation o	f unreacte	ed monome	Ŀ		

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Tab. 2. Polymerization of 1 with cationic catalysts

Tab. 3.	Attempts of vulca	anizing the suppos	sed terpolym	er based on 2 (i.e.	. 8,9-dihydro deriva	tive of 1)	
Run N°	[2] in the feed in mmol 1 ⁻¹	% Unsat. content ^{b)}	$\begin{bmatrix} \eta \end{bmatrix}^{c}$ dl g^{-1}	100% M ^{d)} in kg cm ⁻²	300% M ^{d)} in kg cm ⁻²	T.S. ^{d.e)} in kg cm ⁻²	% E.B. ^{d.f)}
1 ^{a)}	10	0	2,10	2,8 (2,8)	2,4 (1,5)	1,4 (n.d.)	400 (1275)
2 ^{a)}	30	0	1,99	4,1 (3,6)	2,4 (2,1)	2,2 (2,0)	250 (300)
3 ^{a)}	100	0	1,51	Thermal vulcani	zation: 6 h, 145°C	(6	
4 ^{h)}	20	ca. 0,1	1,36	n.d. (4,6)		4,2 (4,6)	65 (115)
S ^{h)}	63	ca. 0,1	1,26	n.d. (3,0)		4 (3)	90 (120)
^{a)} Catal	yst: V(acac) ₃ (C ₂)	$H_5)_2AICI; AI/V =$	8; Solvent: t	oluene; temp.: 0°	Ċ.		
^{b)} IBr a	bsorption.						
e) Tolué	ne, 30°C.						
d) Tensi	le modulus at dif.	ferent elongation:	s; in parenth	leses the value b	before vulcanization	i; n.d.=not deter	minable. Recipe as in
Tab.	ý.						
e) Tensi	le strength.						
n Elong	ation at break.						

⁹⁾ No vulcanization was observed. ^{h)} Catalyst: VCl₄–(C₂H₅)₂AlCl; Al/V = 8; solvent: toluene; temp.: -20°C.

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When the model compound 2, i.e. the 8,9-dihydroderivative of 1 is used as termonomer under typical terpolymerization conditions, the resulting elastomer does not contain unsaturation (IBr absorption) neither it is able to yield a significant amount of crosslinks after sulphur or thermal vulcanization. Such results do not change when the amount of diene 2 in the feed is noticeably increased with respect to the usual concentrations employed for EPTM synthesis (Tab. 3). However, in the presence of acid catalysts, i.e. systems containing strong Lewis acids as VCl₄ or $C_2H_5AlCl_2$, some unsaturation is present in the resulting polymer. This result is due, very likely, to the cationic formation of the polymer of 2 blended with the prevalent portion of EPM.

Therefore, the formation of EPM in the presence of 2 supports the conclusion that the triene 1 enters EPTM chains by selective opening of its norbornenic double bond.

As far as the distribution of 1 along the terpolymer back-bone is concerned, fractionation data reported in Tab. 4 show that unsaturations are distributed homogeneously in the single fractions.

Fraction N ^o	% Weight	$\frac{[\eta]^{a}}{dl g^{-1}}$	$10^{-5} \cdot \overline{M}_{\rm osm}$	wt-% of 1 ^{b)}
1	7,4	2,31	1,30	1,2
2	9,0	2,20	1,29	1,1
3	6,9	2,13	1,21	1,2
4	10,8	1,92	1,18	1,1
5	8,4	2,22	1,11	n.d.
6	8,4	2,19	1,06	1,0
7	8,2	1,44	0,57	1,1
8	10,8	0,91	0,53	1,3
9	10,6	0,32	n.d.	n.d.
10	12,1	n.d.	n.d.	n.d.
Initial sample	100,0	1,65	n.d.	1,39

Tab. 4. Fractionation of a sample of EPTM based on 1

^{a)} Toluene, 30°C.

^{b)} By UV evaluation.

The difference between spectroscopic and radiometric evaluation of termonomer, when a good relationship between the methods holds at low levels of unsaturation, has been taken as the evidence of side reactions concerning the unsaturation of EPDM's^{28,29)} and EPTM's^{3,4,7)}. The use of tritiated **1** has allowed to check only in part the validity of the spectroscopic method used to determine the concentration of unsaturation in EPTM based on 1. In fact, the correlation between the two methods, reported in Fig. 18, shows a high degree of fluctuation, unusual for this kind of relationship¹⁵⁾.



Fig. 18. Relationship between spectroscopic (UV) and radiometric evaluation of 1 with 95% confidence limits

Further investigations are necessary to explain this discrepancy, while Fig. 18 shows that part of 1 is evidenced only by the radiometric method.

The interesting properties of EPTM's based on 1 or its methyl derivatives during the curing process with typical EPDM recipes, are shown in Tab. 5 where some parameters are reported, deduced from the kinetics of vulcanization. The comparison with the behaviours of EPTM's containing the trienes 3 and 4, which can be considered as model compounds of 1 in the sense that they possess some structural features common to the cyclopentadiene system, show clearly that EPTM's containing 1 and methyl derivatives of 1 are very fast curing terpolymers, even at low levels of unsaturation. Tab. 5 collects also some reference data obtained for typical EPDM's vulcanized under similar conditions.

According to Tab. 5 the exceptional reactivity of EPTM's containing a cyclopentadiene ring in the pendant group should be ascribed to the presence of bis-allylic hydrogens typical of this structure. A useful utilization of the enhanced reactivity of this class of EPTM is the possibility of covulcanizing them with highly unsaturated elastomers, e.g. SBR or 1,4-*cis*-polyisoprene⁷).

Conclusions

The triene 1 is able to terpolymerize with ethylene and propylene in the presence of several Ziegler-Natta catalyst systems based on vanadium. Its

1 a n. J.								
Sample	Termono	mer	[n] ^{b)}	t _i c)	TM _{max} ^{d)}	t ₅₀ e)	t an ^{f)}	
å	Type	in wt-%	in dl g ⁻¹	in min	in kg m	in min	in min	
		1,2	3,64	1,33	0,310	4,0	9.33	
2	Mixture ⁹⁾	2,0	2,62	1,00	0,235	1,33	4,0	
3	3	4,1	1,96	1,70	0,256	45,0	168,0	
4	4	5,0 ^{h)}	2,00	2,75	0,230	30,0	139,0	
5	ENB ⁱ⁾	8,1	1,42	3,70	0,470	4,0	31,5	
9	1,4-HD ⁱ⁾	$3,8^{h}$	2,39	6,0	0,535	5,0	35,0	
7	endo-DCP	5,8	2,64	7,2	0,580	18,5	0,66	
^{a)} Recipe ^{b)} Toluei ^{c)} Induct ^{d)} Higher ^{e)} $t_{50} = T$ ^{f)} $t_{90} = T$ ^{g)} Mixtui ^{h)} Appro	e: Polymer = 100; H. ne, 30°C. tion time ¹⁶⁾ st value of the torqu ime requested to re: ime requested to re: ime requested to re: re of mono-, di-, and ximate evaluation b	AF Carbon Black te moment. ach 50% of TM _{ma} ach 90% of TM _{ma} t trimethyl derivat. y iodometric titra sornene; 1,4-HD=	= 50; Circosol-4; ive of 1. tion.	240=5; ZnO=5	; S=2; TMTD=	1; MBT=0,5; te	mp. = 145 °C.	

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distribution along EPTM chains is random and takes place by selective opening of the norbornene double bond of 1. A soluble elastomer can be obtained if no acidity is present in the polymerization medium and the triene concentration in EPTM is <2 wt.-%. Contrarywise, mild cationic catalysts open selectively the conjugated diene system of 1, yielding a soluble homopolymer with a norbornadienic repeating unit, whereas strong Lewis acids furnish an insoluble polymer. Despite of the low amount of unsaturation, EPTM's based on 1 or its methyl-derivatives, are very fast curing and this behaviour has to be attributed to the presence of bis-allylic hydrogens of the cyclopentadiene ring.

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