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temperatures and longer polymerization times than 80 °C and 4 h, respectively, cause the deterioration of the porphyrin and Mg porphyrin moiety in the polymer, as judged from visible absorption spectrum. Values of percent porphyrin or Mg porphyrin moiety in polymer, as determined from absorptivity in $CHCl_3$, were much lower than that (1.5) in the initial vinyl monomer combination, indicating rather poor copolymerizability of Por-D*n* or Mg Por-D*n*. However, since the polymer solutions in DMF were dialyzed against water and the resulting water-insoluble portions (remaining Por-D*n* or Mg Por-D*n* and others) were removed by filtration, the purified polymers contained only copolymerized Por-D*n* or Mg Por-D*n*, which were solubilized in water as a result of copolymerization.

An alternative method consisting of a polymer reaction between copolymer **5** and porphyrin dimer **3** also provided copolymers similar to those by copolymerization (eq 2). The introduction of Mg atom into copolymer **6** could be carried out as in the corresponding Por-D*n*.

The Property of Copolymers. Copolymers of VP with about 1 mol % or less of Por-D*n*, Mg Por-D*n*, and related polymerizable porphyrin dimers were soluble in either water or aqueous organic solvents and are ready for the investigation of their redox functions in aqueous solutions, although the number of porphyrin dimer units per polymer chain could not be determined. VP as comonomer component was selected first for obtaining copolymers soluble in aqueous media and second for activating anionic reactants such as Fast Red A[1] in a function similar to polar aprotic solvents such as *N*-methyl-2-pyrrolidone.[7]

Considering the use of porphyrin and metalloporphyrin dimers, especially as photocatalysts, it may be advisable to bind these functional compound systems to a polymer molecular chain, from the standpoints of easy regulation of structure, solubility, readiness of separation of the catalyst from products, etc.

The results of the functions of these copolymers as photocatalysts, as simulated to photosynthesis in nature, are promising and shall constitute the object of another article.

Registry No. 1, 14609-54-2; Por-D1, 119111-77-2; Por-D2, 119111-83-0; Por-D3, 119111-78-3; Por-D4, 119111-79-4; Por-D5, 119111-80-7; Por-D6, 119111-81-8; Mg Por-D1, 119145-94-7; Mg Por-D2, 119145-96-9; Mg Por-D3, 119145-92-5; Mg Por-D4, 119145-88-9; Mg Por-D6, 119145-93-6; Por-D1/VP (copolymer), 119111-82-9; Por-D2/VP (copolymer), 119111-84-1; Por-D3/VP (copolymer), 119111-85-2; Por-D4/VP (copolymer), 119111-86-3; Por-D5/VP (copolymer), 119111-87-4; Por-D6/VP (copolymer), 119111-88-5; Mg Por-D1/VP (copolymer), 119145-95-8; Mg Por-D1/VP (copolymer), 119145-97-0; Mg Por-D3/VP (copolymer), 119182-72-8; Mg Por-D4/VP (copolymer), 119145-89-0; Mg Por-D6/VP (copolymer), 119145-98-1; VP, 88-12-0; $NH_2CH_2NH_2$, 2372-88-5; $NH_2(CH_2)_2NH_2$, 107-15-3; $NH_2(CH_2)_3NH_2$, 109-76-2; $NH_2(CH_2)_4NH_2$, 110-60-1; $NH_2(CH_2)_5NH_2$, 462-94-2; $NH_2(CH_2)_6NH_2$, 124-09-4; *p*-$MeC_6H_4CH_2Br$, 104-81-4; *p*-$CH_2{=}CHC_6H_4CH_2Cl$, 1592-20-7.

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Synthesis of Syndiotactic Poly-1,2-(4-methyl-1,3-pentadiene)

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ABSTRACT: A homogeneous catalyst which promotes syndiotactic polymerization of styrene has been tested in the polymerization of 1,3-butadiene, isoprene, and 4-methyl-1,3-pentadiene. The first two monomers afford essentially 1,4 cis polymers; from the last monomer the 1,2 syndiotactic polymer is obtained. Catalytic hydrogenation of syndiotactic poly-1,2-(4-methyl-1,3-pentadiene) affords crystalline poly(4-methyl-1-pentene) melting at 186 °C.

Several homogeneous catalytic systems, consisting of titanium or zirconium compounds and methylalumoxane, promote syndiotactic specific polymerization of styrene and substituted styrenes.[1-3] As reported in a previous paper by our laboratory,[4] the same catalytic systems can also promote partially isotactic specific polymerization of propene. However, it has been observed that the organometallic species promoting syndiotactic polymerization of styrene are probably unrelated to those coexisting in the catalytic system, which promote isotactic polymerization of propene.[4-6]

Considering the conjugation of the vinyl group of aromatic monomers in comparison with α-olefins, the next obvious step was to test polymerization of conjugated diolefins, in the presence of a typical catalyst for syndiotactic polymerization of styrene, e.g., tetrabenzyltitanium (IV)/methylalumoxane ($Ti(bz)_4$/MAO). We have polymerized 1,3-butadiene, isoprene, and 4-methyl-1,3-pentadiene in the presence of this catalyst. Polymerizations have been performed, as described in the Experimental Section, under conditions very similar to those usually used for styrene polymerization, excepting we used a milder temperature, which was lowered in order to minimize any chance of cross-linking.

All the diolefins tested gave some polymer, and in Figure 1 are reported the ^{13}C NMR spectra of the three polymers. Comparison of the spectrum of poly(1,3-butadiene) (Figure 1A) with the spectra reported in the literature[7] shows that

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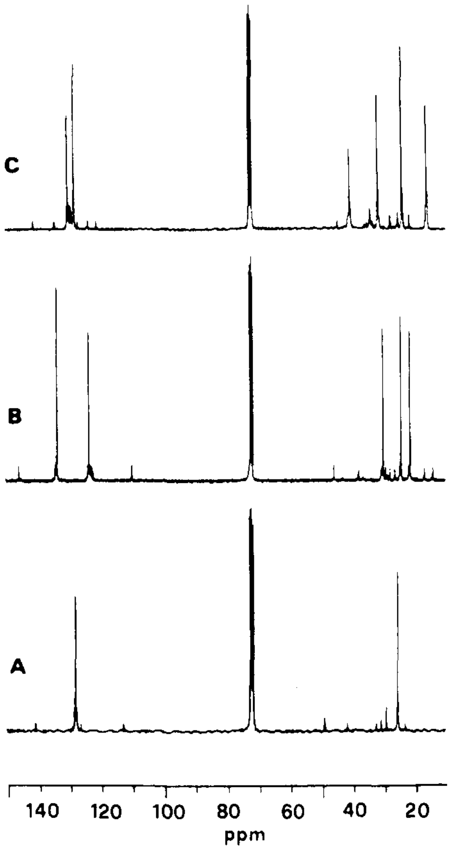
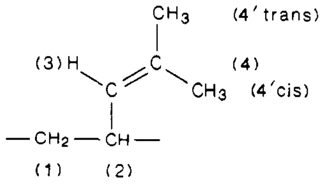


Figure 1. ^{13}C NMR spectra of (A) poly(1,3-butadiene) prepared in the presence of $Ti(bz)_4/MAO$, (B) polyisoprene prepared in the presence of $Ti(bz)_4/MAO$, and (C) poly(4-methyl-1,3-pentadiene) prepared in the presence of $Ti(bz)_4/MAO$. HMDS scale.

the polymer structure is predominantly 1,4 cis (backbone methylene carbons at 25.3_7 ppm and backbone methine carbons at 127.6_2 ppm). Lower intensity resonances observed in the spectrum are due to some 1,2 or 1,4 trans units.[7]

The spectrum of polyisoprene (Figure 1B) consists of five sharp main resonances, showing that this polymer, too, is essentially 1,4. The chemical shift of C-2′ at 21.4_5 ppm is diagnostic of the cis stereochemical structure of the monomer units as reported in the literature.[7] In this case also lower intensity resonances are due to some 1,2 or 1,4 trans units.[7]

The ^{13}C NMR spectrum of poly(4-methyl-1,3-pentadiene) (Figure 1C) consists of five sharp main resonances, which can be assigned to 1,2 monomer units as follows based on the relative intensity of the chemical shift reported in the literature[7,8] for carbons in similar environments and on INEPT ^{13}C NMR experiments;[9] C-1 at 40.4_1 ppm, C-2 at 31.4_7 ppm, C-3 at 129.4_9 ppm, C-4 at 127.4_7 ppm, C-4′ trans at 23.8_4 ppm, and C-4′ cis at 15.9_0 ppm:



The 1,2 structure of the monomer units is consistent with the fact that the chemical shift of the methylene and of one of the methine carbons (C-2) occurs in the region of the saturated carbons, while the chemical shift of the quaternary carbon and of the other methine carbons occurs in the region of the unsaturated carbons. The sharpness of the resonances indicates a stereoregular polymer structure. Lower intensity resonances are partially attributed from the literature[7,8] to 1,4 trans units and to end groups. The 1,2 unit and 1,4 unit contents in the three polymers, measured from the ^{13}C NMR spectra of Figure 1, are reported in Table I. The ^{1}H NMR spectrum of poly-1,2-(4-methyl-1,3-pentadiene), shown in Figure 2, is in agreement with the previous assignment. In addition, it can be observed that the resonance of the protons of the methylene group at 1.3_6 ppm is a false triplet, as expected for a syndiotactic polymer.[10,11]

Table I
1,2 Unit and 1,4 Unit Compositions of the Polymers of Conjugated Dienes

monomer	% 1,2 unit	% 1,4 cis unit	% 1,4 trans unit
1,3-butadiene	5	88	7
isoprene	6	86	8
4-methyl-1,3-pentadiene	≥88	n.d.[a]	n.d.[a]

[a] n.d. = not determined.

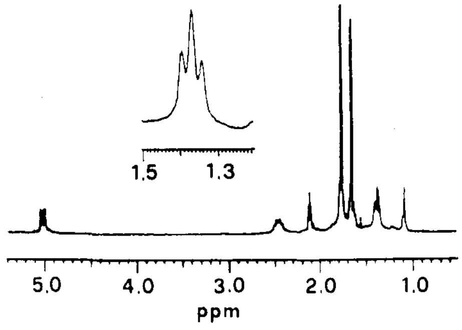


Figure 2. ^{1}H NMR spectrum of poly(4-methyl-1,3-pentadiene) prepared in the presence of $Ti(bz)_4/MAO$. HMDS scale. In the spectrum is also reported the expansion of the resonance of the methylene protons.

The 1,2 structure of poly-1,2-(4-methyl-1,3-pentadiene) can be understood by considering that high substitution of one of the double bonds probably hinders 1,4 addition. The other unsaturation is conjugated and resembles, in reactivity, that of styrene. 2,1 insertion of 4-methyl-1,3-pentadiene could occur for electronic reasons, as is actually reported to occur in the case of styrene.[5,6] The syndiotactic arrangement would result from the steric interactions of the incoming monomer, with the active species entirely similar to those occurring in the polymerization of styrene.[2] In other words, styrene and 4-methyl-1,3-pentadiene resemble each other, having one conjugated unsaturation and being forced to undergo 2,1 insertion, thus giving polymers of similar stereochemical structure. On the other hand, the conjugated unsaturations of 1,3-butadiene and isoprene react preferentially via 1,4 addition on the coordinatively unsaturated transition-metal catalytic complex.

Syndiotactic poly-1,2-(4-methyl-1,3-pentadiene) is amorphous, but catalytic hydrogenation affords a new crystalline fully saturated polymer melting at 186 °C. The X-ray diffraction powder spectrum of this polymer is shown in Figure 3. The predominantly syndiotactic structure of the polymer is an obvious consequence of the structure of the unsaturated starting material. The stereoregularity of the polymer is also confirmed by the sharpness of the resonances observed in the ^{13}C NMR spectrum reported in Figure 4A. Comparison with the spectrum of isotactic poly(4-methyl-1-pentene) (Figure 4B), already reported in the literature,[12] shows appreciable differences in the chemical shifts, expecially for C-1. The chemical shifts of the different carbons of the two stereoregular polymers are reported in the caption of Figure 4.

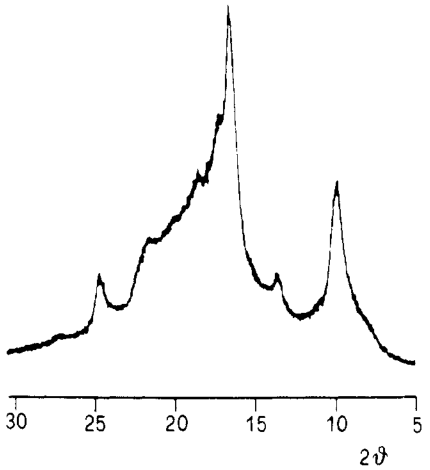


Figure 3. X-ray powder diffraction spectrum of hydrogenated syndiotactic poly-1,2-(4-methyl-1,3-pentadiene), Cu Kα radiation.

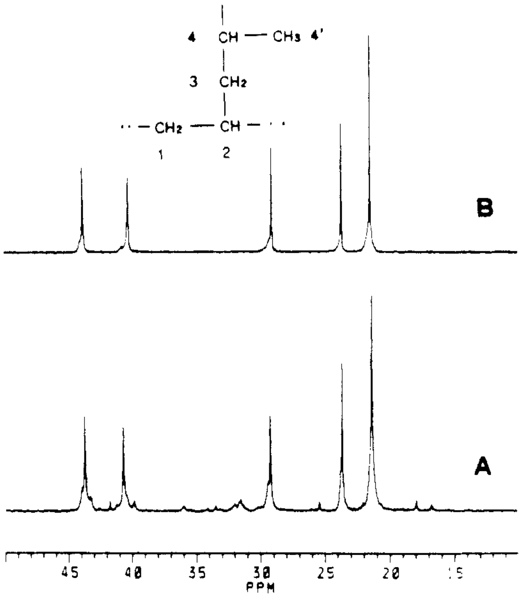


Figure 4. ^{13}C NMR spectra of (A) hydrogenated syndiotactic poly-1,2-(4-methyl-1,3-pentadiene) (C-4′ = 21.3$_0$, C-4 = 23.5$_6$, C-2 = 29.1$_4$, C-1 = 40.6$_0$, and C-3 = 43.6$_3$ ppm) and (B) isotactic poly(4-methyl-1-pentene) (C-4′ = 21.3$_9$, C-4 = 23.5$_8$, C-2 = 28.9$_8$, C-1 = 40.1$_8$, and C-3 = 43.7$_5$ ppm). HMDS scale. The assignment of the carbon resonances is according to the rules of Grant and Paul.[8]

Experimental Section

1,3-Butadiene was purchased from SON Napoli. Isoprene and 4-methyl-1,3-pentadiene were purchased from Fluka A. G. All the monomers were purified by trap-to-trap distillation in the presence of $Al(C_2H_5)_3$. Benzene was purchased from Carlo Erba and dried by boiling in the presence of metallic potassium and distillation under a dry nitrogen atmosphere. $Ti(bz)_4$ and MAO were prepared as previously described.[2]

The polymerizations were performed between 20 and 30 °C, as follows.

Polymerization of 1,3-Butadiene. Thirty-five milliliters of anhydrous benzene was introduced to a 250-mL vial under nitrogen atmosphere. After the inert gas was evacuated, 0.5 mol of 1,3-butadiene was dissolved under vigorous stirring in the benzene, and 1.2 mmol of MAO was introduced. The polymerization was started by introducing 0.012 mmol of $Ti(bz)_4$. After 3 h, the polymerization was stopped by introducing a few milliliters of acidified methanol, and the polymer, coagulated in an excess of methanol, was washed several times and dried in vacuo at room temperature: yield, 0.8 g.

Polymerization of Isoprene. This was performed with the same procedure as the polymerization of 1,3-butadiene using 20 mL of benzene, 0.2 mol of isoprene, 1.2 mmol of MAO, and 0.012 mmol of $Ti(bz)_4$; time, 24 h; yield, 0.05 g.

Polymerization of 4-Methyl-1,3-pentadiene. This was performed with the same procedure as the polymerization of 1,3-butadiene using 5 mL of benzene, 0.1 mol of 4-methyl-1,3-pentadiene, 0.6 mmol of MAO, and 0.006 mmol $Ti(bz)_4$: time, 72 h; yield, 0.5 g.

The hydrogenation of 1.0 g of syndiotactic poly-1,2-(4-methyl-1,3-pentadiene), dissolved in 100 mL of *n*-octane and 1 mL of 1,2,4-trichlorobenzene, was performed in a 250-mL oscillating autoclave immersed in an oil bath thermostated at 150 °C, in the presence of 1.0 g of 10% Pd on charcoal and 45 atm of H_2. After 24 h the polymer solution was filtered over silica and coagulated in ethanol. The melting point of the polymer was measured on annealed samples by a differential scanning calorimeter (Du Pont 9000), at a heating rate of 10 °C/min.

NMR Analysis. The polymers (ca. 20 mg) were dissolved in tetrachloro-1,2-dideuterioethane (ca. 0.4 mL) in 5-mm-i.d. tubes. The ^{13}C and ^{1}H NMR spectra were measured on a AM 250 Bruker instrument operating in the FT mode. The spectra of unsaturated polymers were measured at 300 K, and the spectra of fully saturated polymers were measured at 393 K. Hexamethyldisiloxane (HMDS) was used as an internal reference. The X-ray powder diffraction spectrum of hydrogenated poly-1,2-(4-methyl-1,3-pentadiene) was taken with Cu Kα radiation.

Registry No. $Ti(bz)_4$, 17520-19-3; poly(butadiene), 9003-17-2; polyisoprene, 9003-31-0; poly(4-methyl-1,3-pentadiene), 118456-83-0.

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