Synthesis of New Polymers Containing Porphyrins in Their Side Chains: Radical Polymerizations of 5-[4-(Acryloyloxy)phenyl]-10,15,20-triphenylporphyrin and 5-[4-(Methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin

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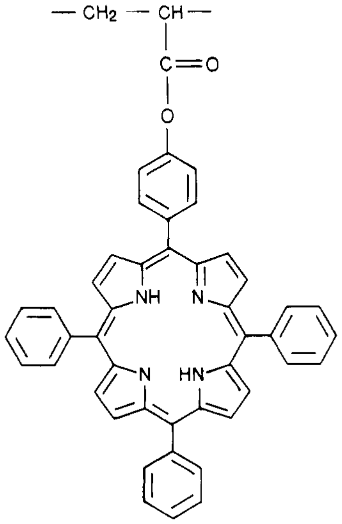
ABSTRACT: Polymers of acrylate and methacrylate containing porphyrin rings in their side chains were obtained by the radical polymerization of 5-[4-(acryloyloxy)phenyl]-10,15,20-triphenylporphyrin (AOTPP) and 5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin (MAOTPP) by using AIBN at 60 °C. PolyAOTPP is composed of a partially crystalline polymer and an amorphous polymer. The former is insoluble in organic solvents, and the latter is soluble in DMF, THF, chloroform, and trifluoroacetic acid; slightly soluble in carbon tetrachloride; and insoluble in ethanol, acetone, hexane, and water. PolyMAOTPP is amorphous and its solubility is similar to that of amorphous polyAOTPP. The visible spectra of polyAOTPP and polyMAOTPP were similar to those of the corresponding monomers, but hypochromism at the Soret band and hyperchromism and a bathochromic shift at 650 nm were observed. The hyperchromism at 650 nm is molecular weight dependent: the higher the molecular weight, the higher the hyperchromism. The observation of hypo- and hyperchromism indicates that the TPP moieties bound to the polymer chain are forced to interact. Thermogravimetric analysis shows that both polymers are thermally stable up to about 400 °C. PolyAOTPP is a semiconductive polymer with electrical conductivity of (6–8) × 10^{-6} S cm^{-1} at room temperature that adsorbs molecular oxygen below 200 K. The copolymerization of MMA (M_1) with MAOTPP (M_2) was performed with AIBN at 60 °C. Monomer reactivity ratios are $r_1 = 0.56 \pm 0.15$ and $r_2 = 0.57 \pm 0.15$, the Q and e values for MAOTPP being 2.03 and 1.47, respectively.

Introduction

Polymers containing paramagnetic species in their side chains are potentially new magnetic materials, because a magnetic ordering of the paramagnetic species through an exchange interaction of unpaired electrons is possible in the polymers.[1-3] We measured the magnetic susceptibility of polymers containing piperadinyloxyl and verdazyl side chain groups and compared their magnetic behavior with those of the corresponding monomers.[4,5] A polymer effect on the magnetic ordering was found in these systems, but the exchange interactions between these organic radicals were too weak for the polymers to function as magnetic materials. Eaton et al.[6] reported an ESR study of spin-labeled silver porphyrins and showed that the silver–nitroxyl exchange interaction was 1000 G. Therefore, we attempted to prepare a polymer containing pendant silver porphyrin and piperadinyloxyl units.

To our knowledge, the radical homopolymerization of vinyl monomers containing a porphyrin moiety in the side chain has not been reported,[7] polymers containing porphyrin moieties are known.[8-14] These polymers have been prepared by the reaction of a prepolymer with porphyrin derivatives,[8,9] by the copolymerization of protoporphyrin[10-13] or heme derivatives[14] with vinyl monomers, and by the condensation polymerization of esters and amines containing the porphyrin moiety.[13] In a preliminary publication, we reported the radical polymerization of 5-[4-(acryloyloxy)phenyl]-10,15,20-triphenylporphyrin (AOTPP) and achieved molecular weights of about 8000.[7]

Recently, we prepared higher molecular weight polyAOTPP by radical polymerization in other solvents. In addition, we found that high molecular weight polymer was obtained by the radical polymerization of 5-[4-(methacryloyloxy)phenyl]-10,15,20-triphenylporphyrin (MAOTPP), the homopolymerization of which was considered to be difficult on the basis of steric repulsion.



In this paper, we report the homopolymerization of AOTPP and MAOTPP, and the copolymerization of MAOTPP with MMA. Some physical and chemical properties of these homopolymers such as heat stability, electric conductivity, and adsorption of oxygen will be presented.

Experimental Section

Materials. Solvents were purified by distillation under nitrogen. MMA and AIBN were purified as described previously.[15] 5-(4-Hydroxyphenyl)-10,15,20-triphenylporphyrin (HOTPP) was prepared from benzaldehyde, *p*-hydroxybenzaldehyde, and pyrrole according to the method of Little et al.[16] (yield, 4.94%). Acryloyl chloride was prepared from acrylic acid and benzoyl chloride as described previously[15] (yield, 34.2%). Similarly, methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride (yield, 85.5%).

AOTPP was synthesized as follows. HOTPP (2.00 g) and triethylamine (0.30 g) were dissolved in 200 mL of THF. The solution was cooled to ice temperature and 0.30 g of acryloyl

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Table I
Radical Polymerization of MAOTPP and AOTPP

polymer	10^2[monomer], mol/dm^{-3}	10^4[AIBN], mol/dm^{-3}	solvent	time, h	conv, %	$\bar{M}_w$
polyMAOTPP	2.54	0.49	DMF	50	18.2	45 000
	11.1	2.18	C_6H_5CN	50	36.7	83 000
polyAOTPP	1.85	1.21	THF	50	28.3	8 000
	9.92	1.72	DMF	50	56.8	69 000
	10.8	15.9	C_6H_5CN	50	49.7	10 000

chloride was added dropwise with stirring over a period of 20 min. The reaction mixture was stirred at room temperature for 2 h after the addition. Removal of the solvent afforded a crude product as an oil, which was then dissolved in chloroform and chromatographed on a silica gel column (20-cm length, 2-cm diameter). AOTPP was isolated by removal of the solvent from the first fraction and dried at 160 °C for 24 h under reduced pressure. yield, 1.53 g (70.4%). mp 300–302 °C; IR (KBr) 1740 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), and 800 ($\delta_{C=C-H}$) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −2.85 (s, 2 H), 6.25 (d, 1 H), 7.10 (d, 1 H), 7.75–8.25 (m, 12 H), 7.75–8.25 (m, 8 H), 8.45–8.82 (m, 8 H), 8.99 (m, 8 H). Anal. Calcd for $C_{47}H_{32}N_4O_2$: C, 82.43; H, 4.71; N, 8.18. Found: C, 82.09; H, 4.69; N, 8.11.

MAOTPP was prepared as follows. HOTPP (4.00 g) and triethylamine (2.00 g) were dissolved in 500 mL of THF. To this solution was added dropwise 2.00 g of methacryloyl chloride with stirring for 20 min, and the reaction mixture was stirred at room temperature for 3 h after addition. Half the solvent was removed by evaporation and the solution was filtered to remove triethylamine hydrochloride. A crude product was isolated as an oily solid by removal of solvent, dissolved in chloroform, and chromatographed on a silica gel column (20 cm). MAOTPP was isolated by removal of solvent from the first fraction and purified by repeated recrystallization from a mixture of chloroform and methanol (10:1 volume ratio). MAOTPP was dried at 60 °C for 24 h under reduced pressure: yield 3.8 g (85.5%); IR (KBr) 1740 ($\nu_{C=O}$), 1630 ($\nu_{C=C}$), 1200 (ν_{C-O}), 800 ($\delta_{C=C-H}$) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −2.82 (s, 2 H), 2.23 (s, 3 H), 5.89 (s, 1 H), 6.65 (s, 1 H), 7.45–7.89 (m, 11 H), 8.25–8.45 (m, 11 H), 8.99 (s, 2 H). Anal. Calcd for $C_{48}H_{34}N_4O_2$: C, 82.50; H, 4.90; N, 8.02. Found: C, 82.57; H, 4.92; N, 7.90.

Radical polymerizations were performed with 2,2′-azobis(isobutyronitrile) (AIBN) at 60 °C. A solution of monomer and AIBN was placed in a glass ampule, degassed, sealed under high vacuum, and polymerized for a given time at 60 °C. A precipitate appeared during the polymerization of AOTPP. The precipitate was separated by filtration. The filtrate was poured into an excess of methanol, and the resulting polymer was isolated by centrifugation and dried at 100 °C. The soluble polymer was purified by three dissolution–precipitation–separation steps from THF–methanol. The molecular weights were estimated by GPC in THF and calibrated against polystyrene standards. The insoluble part was washed 3 times with benzene and dried in vacuo. It was insoluble in organic solvents. The IR spectrum and thermogravimetric analysis were similar to those of the soluble polyAOTPP. The insoluble polymer was partially crystalline as shown by X-ray diffraction. In the case of MAOTPP, no precipitate appeared during the polymerization. Consequently, polyMAOTPP was isolated and purified by the same method.

Copolymerizations of MAOTPP with MMA were performed with AIBN at 60 °C in benzonitrile. The total molar concentration of MAOTPP and MMA was 50 mM, and the AIBN was 0.2 mol % of the monomer concentration. Purification of the copolymers and estimation of the molecular weights were performed as described earlier. Copolymer compositions were estimated by elementary analysis. The monomer reactivity ratios were evaluated according to the Fineman–Ross method.[17]

Measurements. UV–visible spectra were measured in chloroform with a Hitachi 124 spectrometer. IR spectra were recorded in KBr disks. GPC analysis was carried out with a Toyo Soda high-speed liquid chromatograph HGC-810A. Thermogravimetric analysis was performed under a slow stream of nitrogen (30 mL/min) by using a Rigaku Program Temperature-Controller PTC-10 at a heating rate of about 10 °C/min.

The direct-current conductivity was determined by a two-terminal method.[18] A voltage was applied to the two contacts, and the electric current of the circuit and potential difference were measured respectively with a Takeda TR 8651 electrometer and a Takeda 300c high-voltage power supply. The polyAOTPP film for the conductivity measurement was prepared from a 1% benzene solution by spin coating on a Pyrex glass and dried in vacuo for 20 h. The thickness of the film was about 0.22 μm. Gold film electrodes were deposited by evaporation on the surface of the polyAOTPP film.

O_2 adsorption was determined by using a Cahn RH electric microbalance in the temperature range from 77 to 300 K.

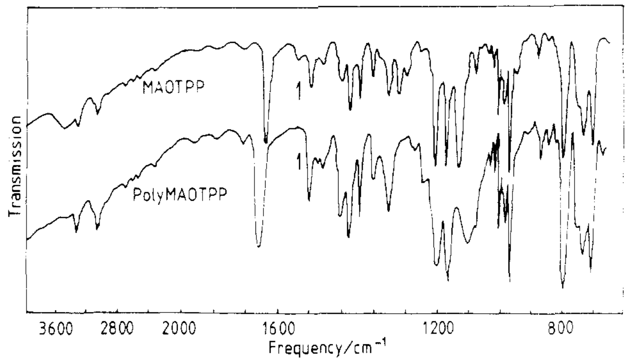

Figure 1. IR spectra of polyMAOTPP and MAOTPP.

Result and Discussion

Radical Polymerization. The radical polymerization of MAOTPP was homogeneous, whereas a precipitate appeared in the polymerization of AOTPP. The precipitate was insoluble in organic solvents. The results of the radical polymerization of AOTPP and MAOTPP are summarized in Table I. Monomer concentration was restricted by the low solubility of these monomers. The molecular weights and yields of the polymers were markedly influenced by the polymerization solvent in the polymerization with similar initiator concentration. For example, AOTPP is more soluble in DMF than in THF. This is possibly attributed to the solubility of monomer.

PolyAOTPP was isolated as a soluble part and an insoluble part. PolyMAOTPP and the soluble part of polyAOTPP were soluble in benzene, chloroform, DMF, THF, and benzonitrile and insoluble in hexane, acetone, ethanol, and water. The IR spectrum of the soluble polyMAOTPP is shown in Figure 1 along with that of MAOTPP. The IR bands of the monomer at 1630 and 1730 cm^{-1} are assignable to the C=C and C=O bonds of unsaturated ester, respectively.[19] On polymerization, the former disappeared and the latter shifted to 1750 cm^{-1}, which is assignable the C=O bond of the saturated ester.[19] Absorption bands characteristic of the porphyrin ring remained unchanged after the polymerization. The IR spectra of polyAOTPP and AOTPP exhibited similar band changes and the IR spectrum of insoluble polyAOTPP was identical with that of the soluble polymer. From the X-ray diffraction shown in Figure 2, it is concluded that the insoluble polymer is partially crystalline. The visible spectra of MAOTPP and polyMAOTPP are shown in Figure 3. MAOTPP has a Soret band at 419 nm and Q bands at 509, 548, 592, and 647 nm.[20] The spectrum of MAOTPP is similar to that of TPP,[2] indicating that the presence of the methacryloyloxy group has no influence

Table II
Radical Copolymerization of MMA (M_1) with MAOTPP (M_2)[a]

	monomer, mol %				copolymer, mol %		
run	[MMA]	[MAOTPP]	time, h	conv, %	[MMA]	[MAOTPP]	$\bar{M}_w \times 10^{-3}$
1	75	25	2	5	70.6	29.4	127
2	66.7	33.3	2.5	10	60.0	40.0	157
3	50	50	4	7	48.2	51.8	105
4	38.5	61.5	3.5	12	44.4	55.6	93
5	33.3	66.7	4	5	41.2	58.8	102
6	25	75	8	6	42.8	57.2	77
7	20	80	10	7	23.7	76.3	71

[a] [MMA] + [MAOTPP] = 50 mM in all runs.

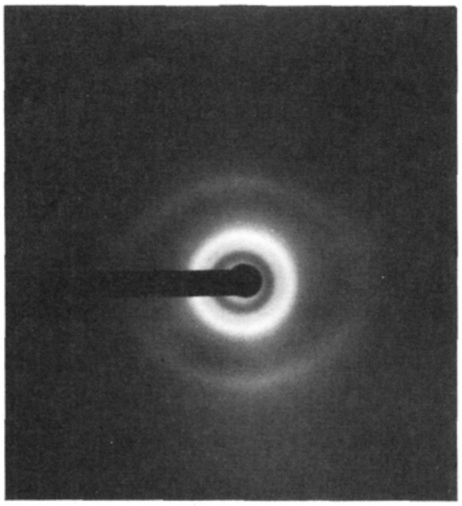

Figure 2. X-ray diffraction pattern for insoluble polyAOTPP powder.

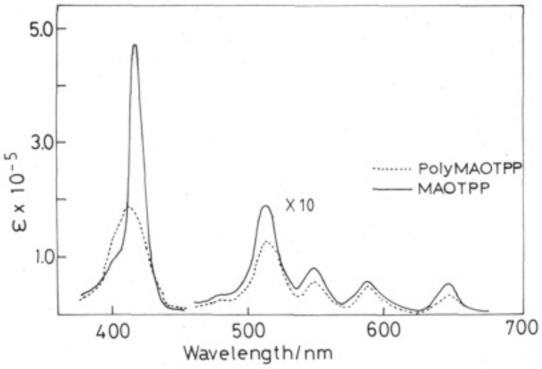

Figure 3. Visible spectra of polyMAOTPP and MAOTPP.

on the absorption of the porphyrin ring. PolyMAOTPP exhibits a Soret band at 415 nm, with the Q bands at 510, 545, 585, and 640 nm. Close examination of these spectra shows that the Soret band of polyMAOTPP is weaker and broader than that of MAOTPP, indicating that the molecular extinction coefficient markedly decreases in the polymer. The molecular extinction coefficients of all the Q bands of polyMAOTPP are slightly lower than those of the monomer. Similar phenomena have been observed for porphyrin dimers in organic solvents[21,22] and explained in terms of an exciton coupling model due to the close approach of the two porphyrin rings.[22] The differences in the spectra between polyMAOTPP and MAOTPP suggest that the TPP moieties bound to this polymer are forced to interact due to their proximity. The visible spectrum of polyAOTPP is shown in Figure 4 along with that of AOTPP. Comparison of both spectra shows that the polymer exhibits at 420 nm (Soret band) a bathchromic shift and hyperchromism at 650 nm. These changes in the spectrum might be ascribed to the change in porphyrin rings due to their chemical reactions with initiating or propagating radicals. For an understanding of the radical reactivity of TPP, radical polymerizations of MMA and styrene (2 M) were performed in the presence of TPP (0.07–0.32 mM), and the molecular weights and yields of the polymers were compared with those obtained in the absence of TPP. No effect of TPP on the radical polymerization of MMA and styrene was found. Accordingly, the differences in the spectra between AOTPP and polyAOTPP also suggest that there is an electronic interaction between the pendant porphyrin moieties in polyAOTPP. The hyperchromism at 650 nm increased with increasing molecular weight. This finding might be correlated with such an electronic interaction between porphyrin moieties.

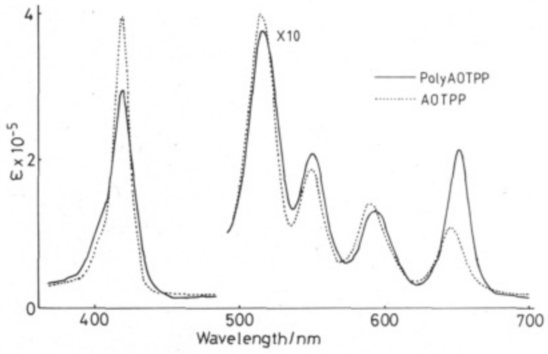

Figure 4. Visible spectra of polyAOTPP and AOTPP.

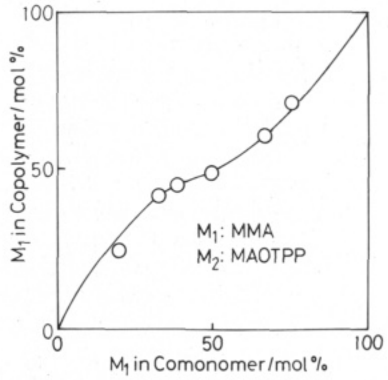

Figure 5. Copolymer composition diagram in the copolymerization of MMA (M_1) and MAOTPP (M_2) at 60 °C.

Copolymerization. In order to gain an understanding of the effect of the TPP ring on the radical reactivity of the vinyl monomers, copolymerizations of MMA (M_1) with MAOTPP (M_2) was performed in benzonitrile at 60 °C with AIBN as an initiator (Table II). The copolymer composition curve is shown in Figure 5. Monomer reactivity ratios were determined to be $r_1 = 0.56 \pm 0.15$ and $r_2 = 0.57 \pm 0.15$ by the Fineman–Ross method,[17] indicating that the radical end of MAOTPP is more reactive toward

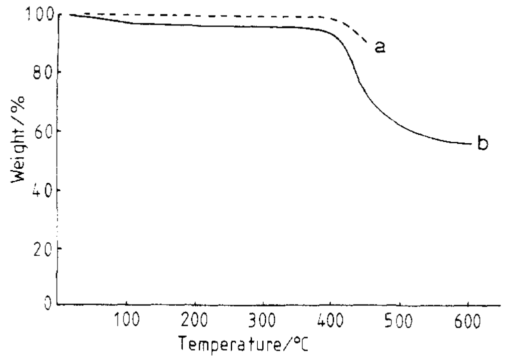

Figure 6. Thermal gravimetric analysis curves for (a) polyAOTPP and (b) polyMAOTPP. The sample was tested in nitrogen gas stream with the rate of 10 °C/min.

Table III
***Q* and *e* Values**

monomer	*Q*	*e*
MAOTPP	2.03	1.47
MMA[a]	0.74	0.40
PMA[a]	1.56	0.73

[a] Reference 22.

MMA than MAOTPP, and that of MMA somewhat more reactive toward MAOTPP than MMA. The *Q* and *e* values for MAOTPP are shown in Table III along with those for MMA and phenyl methacrylate.[23] The *Q* and *e* values are larger than those for PMA and MMA, indicating that the porphyrin ring participates in the resonance stabilization more favorably than the phenyl group and is more electron accepting than the methyl and phenyl groups. No special additional effect of the TPP ring on the radical reactivity of the methacrylate group could be found in the copolymerization, although the polymerization rate of MAOTPP is much lower than that of MMA[24] and phenyl methacrylate.[25] Accordingly, the lower polymerization rate of MAOTPP may be ascribed to the steric repulsion of the TPP rings between the radical end and the attacking monomer.

Physical and Chemical Properties of PolyAOTPP and PolyMAOTPP. Heat Stability. The thermal behavior of polyMAOTPP and polyAOTPP was investigated by thermogravimetric analysis. Results for polyMAOTPP and polyAOTPP are shown in Figure 6. In polyMAOTPP, 3% weight loss occurs between 50 and 100 °C, and little weight loss was observed from 100 to 400 °C. The 3% weight loss below 100 °C is probably due to loss of organic solvents and water. PolyMAOTPP begins to lose weight at ca 400 °C, and 38.5% weight loss occurs at 500 °C. This weight loss is ascribed to thermal decomposition. In the benzene-soluble polyAOTPP, no weight loss was found up to ca 370 °C, and a gradual weight loss started at around 400 °C. The thermogravimetric analysis of insoluble polyAOTPP was similar to that of benzene-soluble polyAOTPP.

Electric Conductivity. The visible spectrum of polyAOTPP showed hypochromism at the Soret band and hyperchromism at 650 nm (Figure 4). This result indicates the presence of an electronic interaction between the TPP moieties in the polymer. Such an electronic interaction might result in enhanced electrical conductivity. The electric current was measured at 20, 100, and 250 V. Results are shown in Table IV. The conductivity of polyAOTPP was determined to be (6–8) × 10^{-6} S cm^{-1}, which is in the region of a semiconductor, and that of polyMAOTPP to be (5–6) × 10^{-8} S cm^{-1}. The electrical measurements were repeated after 1.5-h evacuation at 10^{-3} Torr, and the change in the conductivity was within experimental error.

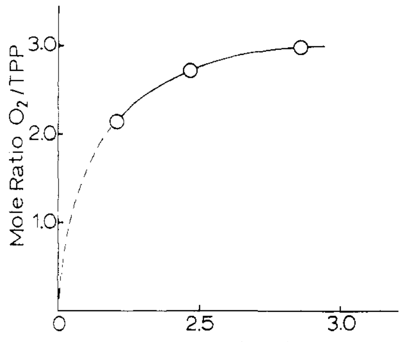

Figure 7. Oxygen adsorption of polyAOTPP as a function of oxygen pressure at 77 K.

Table IV
Electric Currents at Different Potentials of Electrode

polymers	potential, V	electric current, μA
polyAOTPP	20	0.165
	100	0.82 (0.78)[a]
	250	2.35
polyMAOTPP	20	1.22 × 10^{-3} (1.06 × 10^{-3})[a]
	80	4.73 × 10^{-3} (4.25 × 10^{-3})[a]
	250	15.0 × 10^{-3} (13.5 × 10^{-3})[a]

[a] After a 30-min evacuation at 10^{-3} mmHg.

Adsorption of Molecular Oxygen. In the course of a study of the magnetic properties of poly[[5-[4-(acryloyloxy)phenyl]-10,15,20-triphenylporphinato]cobalt(II)] and poly[chloro[5-[4-(acryloyloxy)phenyl]-10,15,20-triphenylporphinato]iron(III)],[26] it was found that polyAOTPP itself adsorbs O_2 in the absence of Co(II) and Fe(III) ions below 200 K.

The weight of polyAOTPP in the presence of O_2 was measured at 77 K. It increased with increasing O_2 pressure and reached a limiting value at pressures higher than 70 Torr, where the molar ratio of O_2 to the TPP moiety was 3. The pressure dependence of the adsorbed O_2 showed a Langmuir-type isotherm as shown in Figure 7, indicating that there is some specific interaction between polyAOTPP and molecular O_2.

In order to understand the nature of the TPP–O_2 interaction, the O_2 adsorption of polyAOTPP was measured at various temperatures under 20 Torr of O_2. The weight of adsorbed O_2 depended on the temperature and reversibly changed with temperature. We can assume an equilibrium for the adsorption process, eq 1 and 2.

$$\text{polyAOTPP---O}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{polyAOTPP} + \text{O}_2 \qquad (1)$$

$$K = \frac{k_1}{k_{-1}} = \frac{[\text{polyAOTPP}][\text{O}_2]}{[\text{polyAOTPP---O}_2]} = \frac{[\text{polyAOTPP}]P_{\text{O}_2}}{[\text{polyAOTPP---O}_2]} \qquad (2)$$

Since the amount of adsorbed O_2 is estimated to be less than 6% of the total O_2 even if polyAOTPP adsorbed O_2 completely, P_{O_2} is assumed to be constant in all experiments. The temperature dependence of K/P_{O_2} is approximately that of K, and thus the binding energy for the O_2 adsorption can be estimated to be 15 KJ mol^{-1}, which corresponds to physical adsorption. Since TPP does not adsorb O_2, the O_2 adsorption of PolyAOTPP is considered to be some type of polymer effect.

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Registry No. MAOTPP, 110528-82-0; poly(MAOTPP), 110528-83-1; AOTPP, 87345-23-1; poly(AOTPP), 87366-09-4; HOTPP, 87345-22-0; MMA, 80-62-6; O_2, 7782-44-7; $H_2C{=}C(CH_3)COCl$, 920-46-7; $H_2C{=}CHCOCl$, 814-68-6.

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Characterization of Functionalized Polymers: Synthesis of Cyanomethylated Polystyrenes and Reaction Chemistry with Palladium(II)

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ABSTRACT: The reactions of linear and cross-linked chloromethylated polystyrenes with NaCN/DMSO have been investigated. Unlike the model compound benzyl chloride, which reacts exclusively by substitution, these functionalized polystyrenes react by substitution and oxidation, producing products bearing both cyanomethyl and aldehyde functional groups. The substrates and reaction products have been fully characterized by solid-state ^{13}C NMR spectroscopy and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, in conjunction with more routine methods. The differences in reactivity of benzyl chloride and chloromethylated polystyrenes are attributed to a matrix effect which is believed to be operative in the case of polymeric substrates. Penetration of the ionic reactant and/or the polar solvent through the nonpolar polymer network is shown to be limited in the case of cross-linked resins by use of electron probe analysis and energy dispersive spectroscopy. An alternative route to cyanomethylated polystyrenes free of aldehyde functionality has been developed. Palladium(II) complexes of polystyrenes bearing cyanomethyl groups have been prepared by displacement of weakly bound nitromethane ligands from solvated palladium(II) precursors. Such complexes are of interest as immobilized promoters and catalysts in organic syntheses.

Introduction

Functionalized polymers have found numerous applications in solid-phase synthesis,[1] as supports in chromatography,[2] as macromolecular ligands for the immobilization of catalytically active metal complexes,[3] and as reagents in organic synthesis.[4]

Despite widespread interest in the chemistry of functionalized polymers there is a paucity of structural and mechanistic data on these solid-phase systems. The problems encountered in acquiring structural and mechanistic data of such materials revolve around the low concentration of functional groups typically encountered and the lack of solubility of cross-linked polymeric systems. These two factors lead to acute analytical problems which eliminate the use of many standard instrumental methods.

We have previously reported[5-10] that structural information may be acquired by the application of solid-state NMR techniques,[11] employing cross-polarization,[12] magic angle spinning,[13] and high-power proton decoupling (CP/MAS NMR), to both inorganic and organic substrates