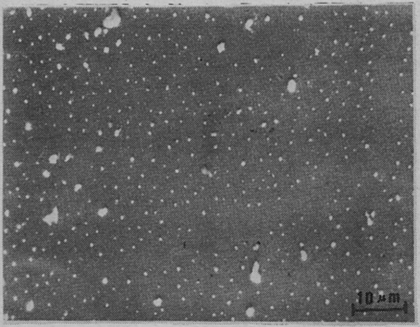

Figure 2. Electronmicrograph of glass slide treated with (PB)Me_2SiOMe (×1400).

poly(butadiene) (II) isolated by precipitation after treating slides were determined by GPC. The $\overline{M}_n$ of the polymer was found to be increased from about 1.8×10^5 to 2.5×10^5 and 3.0×10^5 in two typical experiments whereas the number average molecular weight of the unsilanated poly(butadiene) did not change significantly. An increase in $\overline{M}_n$ and a shift toward doubled $\overline{M}_n$ would be expected if the silanated poly(butadiene) dimerized under reaction conditions in the same way that trimethylmethoxysilane did.[7]

Examination of the slides by optical microscopy (×45) did not reveal any adhering polymer. Significantly different wetting behavior by water was found, however. Drops of water spread uniformly on clean slides, formed regular circular droplets on the slides treated with unsilanated poly(butadiene), and formed irregularly shaped drops on the slides treated with silanated poly(butadienes). Because of the irregular shape of the drops no attempt was made to measure contact angles.

Examination by SEM gave no evidence of adhering polymer on slides treated with the unfunctionalized polybutadiene. On the other hand slides treated with silanated polybutadiene were found to have widely separated discrete particles, about 300 nm in diameter, adhering to them, as shown in Figure 2. The dimensions of these particles are rather larger than those expected for isolated polybutadiene molecules of 150 000–300 000 molecular weight (with a root-mean-square molecular end-to-end distance $(\overline{R^2})^{1/2}$ of about 40–60 nm) and therefore they probably represent aggregates of several polymer molecules. It seems probable that polybutadiene is quite incompatible with glass and does not spread over the surface even when it is chemically bonded by end linking.

Conclusions

Silanated poly(butadiene) having a number-average molecular weight of 150 000 appears to react with triethylsilanol in exactly the same way as the simple silane Me_3SiOMe. The overall reaction can be written:

$$\begin{aligned}&(PB)Me_2SiOMe + Et_3SiOH \rightarrow \\ &\quad (PB)Me_2SiOSiMe_2(PB) + Et_3SiOSiEt_3 + MeOH + \\ &\qquad\qquad (PB)Me_2SiOSiEt_3\end{aligned}$$

Three of these reaction products have been identified directly, and the fourth, the addition product, can therefore be inferred with some confidence.

Similar reactions of silanated poly(butadiene) with OH groups on the surface of glass slides have been inferred from the greater retention of the silanated poly(butadiene) compared to unsilanated poly(butadiene) against washing and the direct observation of microscopic particles, presumably of poly(butadiene), adhering to the glass at widely separated points. These results suggest that poly(butadiene) with a silane end group can be used as a coupling agent to form primary chemical bonds between poly(butadiene) and glass surfaces. An experimental investigation of this system will be reported elsewhere.

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(9) In these initial experiments we were overly concerned about the stability of any polysiloxane bonds that formed and chose the mild washing procedure described above. In later work to be published in connection with adhesion studies, we have washed the slides more vigorously with hot benzene for 24 h in a Soxhlet extractor without destroying the bonds formed with silanated poly(butadiene).

A Procedure for Preparing Aryl Esters of Polyacids. The Conversion of Poly(methacrylic acid) to Poly(phenyl methacrylate)

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ABSTRACT: Poly(methacrylic acid) reacts with excess phenol and phosphoryl chloride to form a copolymer of phenyl methacrylate and methacrylic anhydride. Reaction of this copolymer with sodium phenoxide in phenol yields a phenyl methacrylate–methacrylic acid copolymer that can be converted into essentially pure poly(phenyl methacrylate) by subsequent reaction with phenol and phosphoryl chloride. This process retains the stereochemical integrity of the polymer backbone and can be used to prepare stereoregular poly(aryl methacrylates) from the corresponding poly(methacrylic acids).

One of the most useful polymer analogous reactions known is the alkylation of acidic groups on polymers with diazoalkanes.[1] This reaction has been used extensively in studies on polymer microstructure and reactivity.[2–5] Other

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methods for alkylating polyacids have been reviewed recently.[6] Unfortunately, these processes cannot be used to prepare aryl esters of acidic groups on polymers, and no procedures are presently available for accomplishing such transformations.

The purpose of this paper is to describe a stepwise procedure for converting poly(methacrylic acid) into the corresponding poly(phenyl methacrylate). This procedure was developed to provide a convenient route to isotactic and syndiotactic poly(phenyl methacrylate), but its adaptation for the synthesis of other poly(aryl methacrylates), poly(aryl acrylates), etc., should proceed with little difficulty.

Results and Discussion

Isotactic poly(aryl methacrylates) can be prepared by anionic polymerization techniques,[7] but low yields of relatively low molecular weight materials result, and the reactions are difficult to reproduce. Low-temperature radical-initiated polymerization of aryl methacrylates can, in principle, yield predominantly syndiotactic polymers, but the low percentages of racemic placements in many poly(aryl methacrylates) prepared at 60 °C suggest that the syndiotactic contents of polymers prepared at -78 °C or below will not be particularly high. In fact, there is no reason to expect the racemic placement contents of such polymers to exceed that of poly(methyl methacrylate) prepared under similar conditions. The poly(methyl methacrylate) with the highest syndiotactic content has been prepared by methylating highly syndiotactic poly(methacrylic acid) rather than by direct polymerization.[8]

In view of the above considerations, we concluded that the best route to high molecular weight isotactic and syndiotactic poly(aryl methacrylates) would be through chemical modification of the corresponding poly(methacrylic acids). Thus, isotactic poly(methacrylic acid) of high molecular weight and high steric purity can be prepared by hydrolysis of isotactic poly(methyl methacrylate).[9,10] Predominantly syndiotactic poly(methacrylic acid) can be prepared by radiation-induced polymerization of methacrylic acid in isopropyl alcohol at low temperatures.[8]

The development of a procedure for converting poly(methacrylic acid) into poly(phenyl methacrylate) was made difficult by the limited number of solvents that would be suitable for the reaction and be compatible with the starting, intermediate, and final polymers. Poly(methacrylic acid) is soluble in water and some hydroxylic solvents. These would compete with phenol in esterification attempts, and they are not good solvents for poly(phenyl methacrylate). An additional difficulty was that many attempts to activate the acid groups on poly(methacrylic acid) for reaction with phenol led to gelation, presumably due to the formation of intermolecular anhydride cross-links. Thus, attempts to prepare poly(methacryloyl chloride) by the reactions of poly(methacrylic acid) with thionyl chloride or phosphoryl chloride resulted in heterogeneous reaction mixtures. An attempt to couple poly(methacrylic acid) with phenol using diphenylcarbodiimide met a similar fate. [Klesper and Strasilla[11,12] have recently been successful, however, in using dicyclohexylcarbodiimide to couple alcohols with poly(methacrylic acid) in the presence of tertiary amines, in conversions up to 60%.]

$$[\text{-CH}_2\text{C(CH}_3\text{)(COOH)-}]_m \rightarrow [\text{-CH}_2\text{C(CH}_3\text{)(COCl)-}]_m$$

$$[\text{-CH}_2\text{C(CH}_3\text{)(COOH)-}]_m + \text{PhOH} + \text{PhN=C=NPh} \rightarrow [\text{-CH}_2\text{C(CH}_3\text{)(COOPh)-}]_m + \text{PhNHCONHPh}$$

The difficulties mentioned above were surmounted by coupling poly(methacrylic acid) with excess phenol in the presence of $POCl_3$.[13,14] Phenol containing a small amount of pyridine proved to be a good solvent for initial, intermediate, and final products, and its presence in large excess served to minimize intrachain reactions as well as to destroy intermolecular anhydride cross-links that did form.

$$[\text{-CH}_2\text{C(CH}_3\text{)(COOH)-}]_m + 3\text{PhOH} + \text{POCl}_3 \xrightarrow{95\ ^\circ\text{C}} [\text{-CH}_2\text{C(CH}_3\text{)(COOPh)-}]_m + 3\text{HCl} + (\text{PhO})_2\text{P(O)OH (and other phosphate esters)}$$

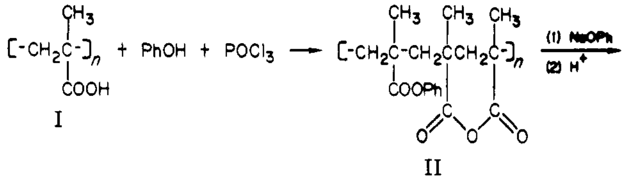
The reaction is believed to involve preferential reaction of the acid groups on the polymer with $POCl_3$ to form either acid chloride or mixed anhydride groups, which then react with phenol to establish the ester linkage.

$$\text{RCOOH} + \text{POCl}_3 \rightarrow \text{RCOCl} \xrightarrow{\text{PhOH}} \text{RCOOPh} + \text{HCl}$$

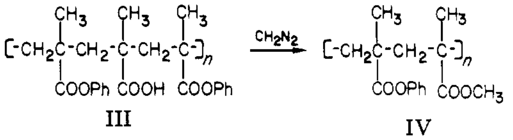
$$\text{RCOOH} + \text{POCl}_3 \rightarrow \text{RCOOPOCl}_2 \xrightarrow{\text{PhOH}} \text{RCOOPh} + \text{HOPO(OPh)}_2$$

Since phenol can compete with carboxylic acids for reaction with $POCl_3$, an excess of $POCl_3$ was employed.

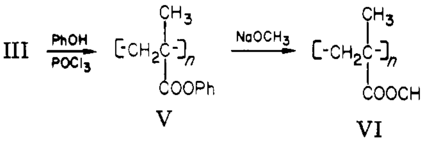
The product first obtained from the poly(methacrylic acid)–phenol–$POCl_3$ reaction was shown by a number of methods to be a copolymer containing phenyl methacrylate and methacrylic anhydride units (II). Thus, the infrared spectrum of the polymer contained a band at 1798 cm^{-1} that can be attributed to the anhydride structure. No absorption was evident at 1702 cm^{-1}, indicating that all carboxyl groups had been consumed. Reaction of the copolymer with sodium phenoxide, followed by acidification, yielded a product that did not absorb at 1798 cm^{-1}, but that absorbed strongly at 1702 cm^{-1}. This was considered to be a phenyl methacrylate–methacrylic acid copolymer (III).


I II

$$[\text{-CH}_2\text{C(CH}_3\text{)(COOH)-}]_n + \text{PhOH} + \text{POCl}_3 \rightarrow [\text{-CH}_2\text{C(CH}_3\text{)(COOPh)-CH}_2\text{C(CH}_3\text{)CH}_2\text{C(CH}_3\text{)-}]_n\ (\text{anhydride } \text{-C(=O)-O-C(=O)-}) \xrightarrow[\text{(2) H}^+]{\text{(1) NaOPh}}$$


III IV

$$[\text{-CH}_2\text{C(CH}_3\text{)(COOPh)-CH}_2\text{-C(CH}_3\text{)(COOH)-CH}_2\text{-C(CH}_3\text{)(COOPh)-}]_n \xrightarrow{\text{CH}_2\text{N}_2} [\text{-CH}_2\text{C(CH}_3\text{)(COOPh)-CH}_2\text{-C(CH}_3\text{)(COOCH}_3\text{)-}]_n$$


III V VI

$$\text{III} \xrightarrow[\text{POCl}_3]{\text{PhOH}} [\text{CH}_2\text{C(CH}_3\text{)(COOPh)-}]_n \xrightarrow{\text{NaOCH}_3} [\text{-CH}_2\text{C(CH}_3\text{)(COOCH}_3\text{)-}]_n$$

The phenyl methacrylate–methacrylic anhydride copolymer (II) was analyzed by 60 MHz ^{1}H NMR spectroscopy. Comparison of the aromatic and aliphatic proton resonance areas indicated that 22–25% of the original acid units had formed anhydride groups when either atactic or syndiotactic poly(methacrylic acid) was used as starting material (I). When the starting material was isotactic poly(methacrylic acid), 36% of the acid units were involved in anhydride groups. These results were consistent with the intensities of the anhydride carbonyl absorptions in the infrared spectra of these polymers. In addition, the atactic phenyl methacrylate–methacrylic acid copolymer (III) was methylated with diazomethane[1] and the resulting

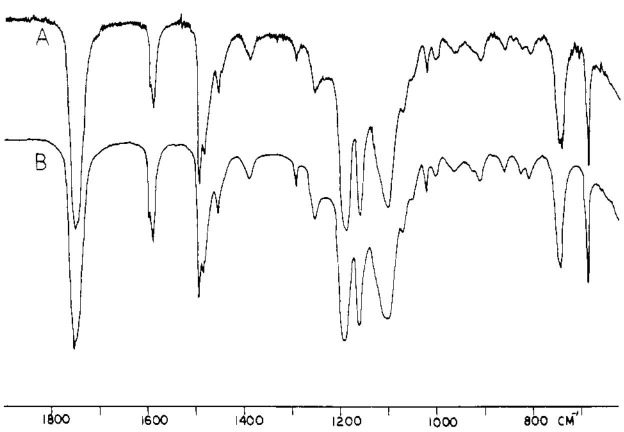


Figure 1. IR spectra of directly (A) and indirectly (B) prepared poly(phenyl methacrylate). Films cast from $CHCl_3$

phenyl methacrylate–methyl methacrylate copolymer (IV) was shown by NMR analysis to contain 11.5% methyl methacrylate units. This result is entirely that expected according to the transformation of II → III → IV depicted above.

The presence of cyclic anhydride structures in the products of the polyacid–phenol–$POCl_3$ reactions is not surprising in view of the great tendency of such structures to form in other polymer modification reactions.[11,12,15-18] However, this tendency precluded a direct one-step synthesis of poly(phenyl methacrylate) from the corresponding polyacid. A control experiment involving the treatment of poly(phenyl methacrylate) with $POCl_3$ indicated that poly(phenyl methacrylate) was stable to the conditions of the phenylation reaction. It, therefore, seemed reasonable to convert the anhydride units to phenyl ester units. The phenyl methacrylate–methacrylic anhydride copolymer (II) was then converted to a phenyl methacrylate–methacrylic acid copolymer (III) by reaction with sodium phenoxide. This copolymer was then rephenylated via the phenol–$POCl_3$ reaction. Infrared analysis of an intermediate product from this reaction showed a decrease in the intensity of the carbonyl band at 1702 cm^{-1} and the appearance of an absorption at 1802 cm^{-1} which can be attributed to the acid chloride structure. Since the acid groups in III could be expected to be essentially free from acid neighbors, cyclization was not expected to be a significant side reaction in the second phenylation reaction. This proved to be the case, and the product (V) was a polymer whose infrared and ^1H NMR spectra were essentially identical to those of poly(phenyl methacrylate) prepared directly from the monomer. Figure 1 compares, for example, the infrared spectra of atactic poly(phenyl methacrylates) prepared directly from the monomer and derived from atactic poly(methacrylic acid). To insure that all phenyl groups present were in phenyl ester linkages and that no side reactions had gone undetected, poly(phenyl methacrylate) (V) was transesterified with excess sodium methoxide in dioxane. The resulting poly(methyl methacrylate) (VI) was analyzed by 60 MHz ^1H NMR spectroscopy and was found to contain no phenyl groups.

Table I compares the isotactic (*mm*), heterotactic (*mr* + *rm*), and syndiotactic (*rr*) contents of poly(methyl methacrylate) and poly(phenyl methacrylate) samples derived from atactic, isotactic, and predominantly syndiotactic poly(methacrylic acid). These were measured from the α-methyl proton resonance patterns of the polymers. Since the same configurational structures are evident for both polymers and since the methylation of poly(methacrylic acid) is known to proceed with retention of the configurational structure of the polymer, the same conclusion can be drawn concerning the phenylation process. The molecular weights of poly(methyl methacrylate) and poly(phenyl methacrylate) derived from atactic poly(methacrylic acid) were determined from viscosity measurements. The degree of polymerization of poly(methyl methacrylate) was 1250, while that for poly(phenyl methacrylate) was 1175. Since essentially the same degrees of polymerization are evident for both polymers it can be concluded that chain degradation does not accompany the phenylation process. This process should also be applicable to the preparation of other aryl esters of polyacids.

Table I
Distributions of Configurational Dyads in Poly(methyl methacrylate) and Poly(phenyl methacrylate) Derived from Poly(methacrylic acid)

polymer	*fmm*	*f*(*mr* + *rm*)	*frr*
atactic poly(methyl methacrylate)	0.05	0.36	0.59
atactic poly(phenyl methacrylate)	0.06	0.35	0.59
isotactic poly(methyl methacrylate)	1.00	0.00	0.00
isotactic poly(phenyl methacrylate)	1.00	0.00	0.00
syndiotactic poly(methyl methacrylate)	0.00	0.09	0.91
syndiotactic poly(phenyl methacrylate)	0.00	0.11	0.89

Experimental Section

Poly(methacrylic acids). Atactic poly(methacrylic acid) was prepared by bulk polymerization at 60 °C using AIBN as the initiator. Predominantly syndiotactic poly(methacrylic acid) was prepared by submitting a 20% solution of the monomer in isopropyl alcohol to ^{60}Co γ radiation (3.6×10^6 rad/mol) at −78 °C.[6] The atactic and predominantly syndiotactic polymers were reprecipitated from methanol solution into hexane and were dried in vacuo. Isotactic poly(methacrylic acid) was prepared by hydrolysis of isotactic poly(methyl methacrylate)[7,8] in concentrated H_2SO_4 at room temperature (6 days). The polymer was obtained by pouring the reaction mixture into distilled water and was exhaustively washed with water until the washings were neutral. It was dried in vacuo to constant weight. Samples of these polymers were methylated with diazomethane, and the resulting polymers were characterized by 300 MHz ^1H NMR spectroscopy (Table I).

Phenylation Procedure. A mixture of finely ground poly(methacrylic acid) (0.30 g, 0.0035 mol), phenol (50 mL), and a few drops of dry pyridine was heated at reflux until a homogeneous solution was obtained. The solution was then allowed to cool to 95 °C, and the polymer remained in solution. Alternatively, a sample of a phenyl methacrylate–methacrylic acid copolymer (0.57g, 0.0035 mol) was heated for several hours, with stirring, at 95 °C until a homogeneous solution was obtained. While maintaining heating and stirring, $POCl_3$ (2.00 g, 0.0130 mol) was added in five equal portions at hourly intervals. The orange reaction mixture was then stirred for an additional 12 h and approximately one-half of the excess phenol was removed by vacuum distillation. The hot solution was then poured into 20 volumes of methanol to precipitate the polymer as a white powder. This was collected, washed with methanol, and dried. The yield was essentially quantitative in all cases (e.g., 0.52 g, when poly(methacrylic acid) was the starting material). The product was then reprecipitated from acetone solution into methanol and dried in vacuo.

When phenyl methacrylate–methacrylic acid polymer was the starting material, the amount of $POCl_3$ employed was twice that mentioned above.

Poly(phenyl methacrylate) that had been prepared directly from its monomer was submitted to this procedure. The material recovered was identical to the starting material, as judged by a comparison of their infrared and ^1H NMR spectra.

Reaction of Partially Phenylated Polymer with Sodium Phenoxide. Finely divided product obtained from the poly(methacrylic acid)–phenol–$POCl_3$ reaction (0.57 g, 0.0035 mol) was added to phenol (50 mL), and the mixture was heated with stirring at 95 °C until it became homogeneous. This required less than 1 h. Freshly cut sodium metal (0.40 g, 0.018 mol) was then added, and the resulting pink reaction mixture was heated at 95 °C and stirred for 1.5 h. Approximately one-half of the excess phenol was then removed by vacuum distillation. The concentrated reaction mixture was allowed to cool to 40 °C and concentrated HCl (10 mL) was added, slowly, with stirring. The resulting suspension was poured into 20 volumes of methanol to precipitate the polymer, which was then washed with methanol and dried in vacuo. The yield was 0.54 g. Most of this sample was rephenylated, using the procedure described above, but a portion of it was reprecipitated from acetone into methanol, and then dried in vacuo. The infrared spectrum of this portion contained a strong absorption band at 1702 cm^{-1}. A portion of this sample was methylated with diazomethane.[1] The ^{1}H NMR spectrum of the resulting product contained a strong resonance at ~3.5. Its intensity indicated that approximately 11.5% of the units were methyl methacrylate units.

Characterization of the Completely Phenylated Polymer (V). The $POCl_3$–phenol and $NaOC_6H_5$–phenol reactions were conducted once more to obtain a material that analyzed satisfactorily for poly(phenyl methacrylate).

Anal. Calcd for $(C_{10}H_{10}O_2)_n$: C, 74.06; H, 6.22; Cl, 0.00; P, 0.00. Found: C, 74.12; H, 6.34; Cl, <0.05; P, <0.05.

The infrared spectrum of atactic poly(phenyl methacrylate) derived from atactic poly(methacrylic acid) is compared in Figure 1 with the spectrum of poly(phenyl methacrylate) derived directly from the monomer.

Reaction of Completely Phenylated Polymer with Sodium Methoxide. Finely divided product obtained from the phenylation of the atactic phenyl methacrylate–methacrylic acid copolymer (0.16 g, 0.0010 mol) was added to degassed dioxane (30 mL) under nitrogen, and the mixture was heated with stirring at 50 °C until it became homogeneous. This required 1 h. Degassed methanol (3.2 g, 0.10 mol) was added dropwise during 1 h. Freshly cut sodium metal (0.25 g, 0.01 mol) was then added, and the resulting reaction mixture was heated at 50 °C, under nitrogen and stirred for 24 h. The reaction mixture was allowed to cool to room temperature and was poured into 20 volumes of methanol to precipitate the polymer as a white powder. The yield was essentially quantitative (0.093 g, 0.00093 mol). The polymer was reprecipitated from acetone into methanol, and then dried in vacuo. The ^{1}H NMR spectrum of this polymer contained no resonances assignable to aromatic protons.

Viscosity Measurements. Intrinsic viscosities were determined in acetone solution at 25 °C using a Ubbelohde dilution viscometer. The viscosity-average molecular weights were calculated by the relationships given for poly(methyl methacrylate) by Meyerhoff and Schulz[19] and for poly(phenyl methacrylate) by Hadjichristidis and co-workers.[20] Degrees of polymerizations were calculated by dividing the viscosity-average molecular weights of the polymers by the molecular weights of the respective monomers.

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N-Substituted Poly(α-amino acids). 1. Synthesis and Characterization of Poly(*N*-methyl-γ-methyl L-glutamate) and Poly(*N*-methyl-γ-ethyl L-glutamate)[1]

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ABSTRACT: The synthesis of high molecular weight poly(*N*-methyl-γ-methyl L-glutamate) and poly(*N*-methyl-γ-ethyl L-glutamate) has been performed by permethylation of poly(γ-methyl- and γ-ethyl L-glutamate). Among the various techniques known for low molecular weight materials, only the procedure introduced by Lederer's group[2a] proved workable in the case of high molecular weight substrates. The degree of methylation was always higher than 95% as shown by elemental analysis, amino acid analysis, and IR techniques. Attempts to obtain polymers starting from N-substituted NCAs other than proline NCA, sarcosine NCA, and *N*-methylalanine NCA failed in all cases. The N-methylated polymers are readily soluble in dimethylformamide, 2,2,2-trifluoroethanol, tetrahydrofurane, and methylene chloride, while they sparingly dissolve in water and methanol. Preliminary CD measurements suggest that the above N-methylated polypeptides adopt an all-trans conformation in solvents such as TFE, methanol, and water.

N-substituted polypeptides exhibit very interesting conformational properties, due to the lack of hydrogen bonding and to the possibility of cis and trans isomerism around the peptide bond. It is well known that poly(L-proline) can exist in two forms. Form I is a rather compact right-handed helical structure containing all cis peptide bonds.[2b–4] Isomerization to trans amide configuration leads to poly(L-proline) II, whose structure is a rather extended