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Chemical Modification of Poly (Methyl Acrylate) via Metalation and α - Substitution

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SUMMARY

Poly(methyl acrylate) was transformed into polymers containing α-substituted units by a two-step reaction sequence involving formation of a poly(enolate) by base abstraction of the hydrogens located α to the ester carbonyl groups, followed by reaction of the poly(enolate) with electrophiles such as carbon dioxide, sulfur dioxide, or ethyl bromoacetate. Further modification of the α-carboxylate or α-sulfinate polymers led to poly(acrylates) bearing α-methyl carboxylate, α-methyl sulfone, or α-(2-hydroxyethyl sulfone) functional groups. Quenching of the poly(enolate) with ethyl bromoacetate gave a polymer containing itaconate as well as acrylate units. In general, the degree of functionalization achieved was from 0.3 to 0.65.

INTRODUCTION

Functionally modified polyacrylates have important technological applications. For example, α-substituted polyacrylates have interesting chemical and physical properties which, among other applications, make them suitable for use as lithographic resists [HALLER et al. 1968, THOMPSON et al. 1973, HATZAKIS 1979, PITTMAN et al. 1980, WILLSON et al. 1981, ITO et al. 1982]. Unfortunately some of the α-substituted polyacrylates are difficult to obtain in sufficient quantity to allow full characterization or functional evaluation. The α-carboxymethyl and α-sulfonylalkyl acrylates, for example, have structural characteristics that warrant testing for resist applications but the monomers are available only via laborious multistep syntheses [Org. Syn. Coll. Vol. IV, 298, GIPSTEIN et al. 1980] and the polymerizations are difficult to control because of the extreme reactivity of the monomers.

Preparation of substituted polyacrylates by chemical modification has been reported but these modification reactions have been restricted to transformations at reactive pendant groups. For example, poly(glycidyl methacrylate) has been reacted with amines to provide a polymer with pendant amino-alcohol groups [SVEC et al. 1977] and with periodate to afford the corresponding aldehyde containing polymer [SVEC et al. 1978]. We recently reported the synthesis of certain poly(olefinsulfone)s via a chemical

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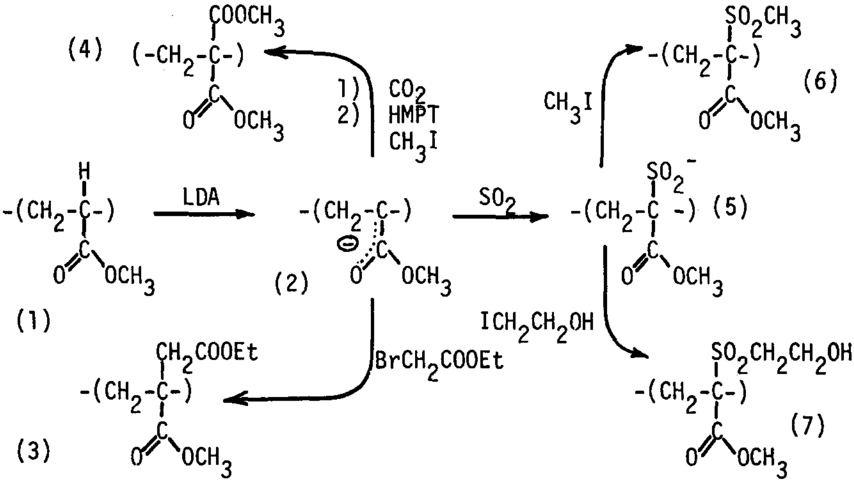
modification sequence that involves substitution on the backbone and allows access to polymeric structures that are otherwise difficult or impossible to obtain [FRECHET et al. 1982]. A similar conceptual approach involving polymer modification at the backbone has recently been reported [ESPENSCHEID and SCHULTZ 1981] wherein N-substituted polyamides were prepared by metalation and alkylation of unsubstituted polyamide precursors. We now report the progress of our efforts directed toward chemical modification of polyacrylates through direct substitution on the backbone.

RESULTS AND DISCUSSION

The poly(alkyl acrylate)s are, in one respect, analogous to the poly(olefinsulfone)s. That is, the acidity of certain protons on the backbone is higher than those on the side chain and, in particular, the α-proton is several orders of magnitude more acidic than any other. Consequently, in a route analogous to that used to successfully modify the backbone of poly(olefinsulfone)s and polyamides, one can consider exclusive removal of the α-hydrogen under suitable basic conditions followed by quenching of the resulting poly(enolate) with electrophiles to achieve convenient access to α-substituted poly(alkyl acrylate)s.

The alkylation of esters in their α position is a well-known reaction [MARCH 1977] which is usually best carried out by quantitative generation of the ester enolate using a strong, hindered base such as lithium isopropylcyclohexylamide [RATHKE and LINDERT 1971] or lithium diisopropylamide (LDA) [CREGGE et al. 1973] followed by quenching of the enolate with an alkyl halide at low temperature.

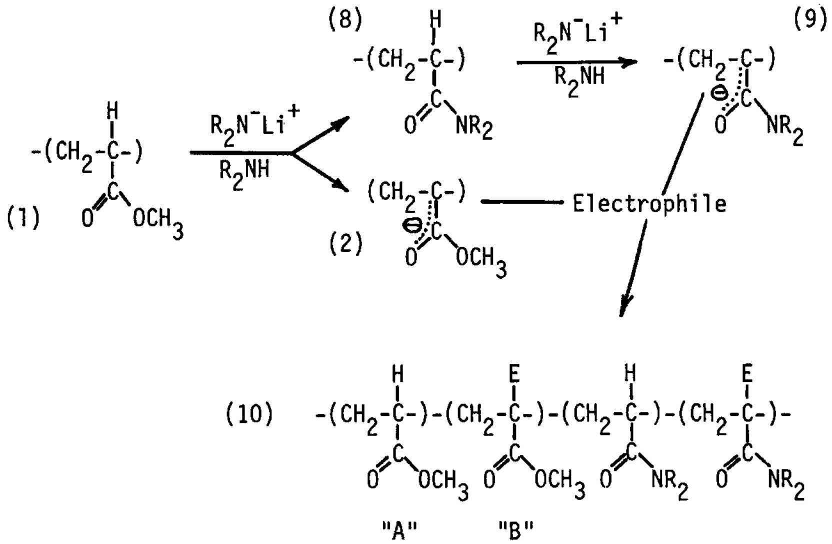


SCHEME I: Chemical Modification of Poly(methyl acrylate)

The potential use of this reaction for the chemical transformation of poly(methyl acrylate) into its α-substituted analogs was tested as shown in Scheme I.

A THF solution of poly(methyl acrylate) (1) was treated with lithium diisopropylamide at low temeprature to generate the corresponding poly(enolate) (2) which was then treated with various nucleophiles to afford α-substituted derivatives of (1). For example, quenching of (2) with an excess of ethyl bromoacetate gave polymer (3) in which a significant proportion of the α hydrogens had been replaced resulting in the formation of a copolymer containing both acrylate and itaconate units. Examination of the proton and carbon NMR spectra of (3) confirms that approximately 65% of the repeating units in the final polymer were itaconate. Thus, the 13-C NMR spectrum of (3) included two ester carbonyl peaks (175 and 170 ppm), signals corresponding to both of the ethyl ester carbons (60 and 13 ppm) and methyl ester carbons (51 ppm).

The introduction of methyl carboxylate groups in the α positions of (1) was carried out by quenching enolate (2) with excess carbon dioxide followed by treatment with iodomethane in HMPT to give the functionalized polymer (4). The second step of this reaction is exothermic and accompanied by evolution of gas suggesting that some decarboxylation takes place during the esterification. The 13-C NMR spectrum of (4) was markedly different from that of (1) with two distinct ester carbonyl peaks (171 and 175 ppm) in approximately 4:3 ratio, and two strong methyl ester signals (52 and 53 ppm). Additional data suggested that approximately 40% of the acrylate units have been modified. The preparation of polymers (6) and (7) containing α-alkyl sulfonyl groups was achieved by a two-step reaction sequence involving first, the formation of a polymeric sulfinate (5) and, in the second step, the reaction for the nucleophilic sulfinate groups with appropriate alkyl halides. Reaction of the polymeric enolate (2) with excess sulfur dioxide to form the sulfinate (5) was best accomplished by adding liquid sulfur dioxide to the enolate rather than bubbling SO_2 gas through the polymer suspension. After reaction of (5) with excess iodomethane or 2-halo-ethanol, analysis of polymers (6) and (7) shows a 35-55% degree of substitution in several preparations. NMR and IR studies of (6) and (7) confirmed that the expected substitution had indeed occurred. Thus, the 13-C NMR spectrum of (6) has a sharp methylsulfonyl signal (48 ppm), two methyl ester signals of approximately equal intensity (52 and 53 ppm) and two ester carbonyl signals (172 and 175 ppm) in approximately 1:1 ratio. The infrared spectrum of (6) includes sulfone bands at 1310 and 1135 cm^{-1}, and difference FT-IR spectroscopy on polymers (6) and (1) reveals the presence of additional methyl absorptions at 1374 and 2957 cm^{-1} for polymer (6).



SCHEME II: Side Reactions

As detailed above, the modified polymeric products can be assigned a structure consistent with α-substitution albeit at less than complete conversion. However, in every case the NMR spectra of the products exhibit low intensity resonances that are difficult to reconcile by structure or sequence arguments and the products contain small and variable amounts of nitrogen by combustion analysis. We believe that both the nitrogen incorporation and the spurious resonances arise from a side reaction that results in amide formation. That is, a side reaction that results from reaction of LDA or diisopropylamine with the pendant ester group (Scheme II). The amidated units (8) can, in turn, be deprotonated by reaction with LDA and the corresponding enolate (9) is then subject to alkylation. Thus, the structure of the final polymer product is rendered very complex through various sequences of amidation, enolate formation and subsequent electrophilic substitution (10).

The extent of the side reaction ranges from 5-7% in the formation of (3) to as much as 35% in certain preparations of (7) as determined from nitrogen combustion analytical data. In general, the extent of amidation is far greater (23-35%) in preparation of 6 and 7 than it is in preparation of either 3 or 4 (less than 10%). It is likely that the more drastic conditions required for formation of 5, 6 and 7 are responsible for the increased extent of nitrogen incorporation.

In attempt to suppress the amidation side reaction during chemical modification, a more hindered base than LDA was tested. The anion of 2,2,6,6-tetramethylpiperdine was used to prepare 7. The resulting product contains only traces of nitrogen and the NMR spectrum is clean and consistent with the proposed structure. The degree of functionalization achieved with the more hindered base is lower (35%) than that achieved with LDA (55%) but no attempt has been made, as yet, to optimize the reaction conditions.

We are continuing to pursue this interesting reaction sequence and several schemes for improving the degree of substitution while suppressing the amidation are being tested. These include a study of tert-butyl acrylates instead of 1, and of copolymers such as poly(alkyl acrylate-co-alkyl methacrylate). Nearly complete substitution is probably required for optimum functional utility in lithographic resist applications as poly(alkyl acrylates) are known to behave as negative (cross linking) resists under e-beam exposure while the α-substituted counterparts are, in general, positive resists.

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EXPERIMENTAL

NMR spectra were measured on Varian HA-100 or CFT-80 spectrometers. IR spectra were obtained using a Nicolet MX-1 FT-IR or a Perkin-Elmer Model 281 spectrometer. Elemental analyses were performed by MHW laboratories or at the University of Ottawa. Tetrahydrofuran was dried over lithium aluminum hydride and distilled immediately before use. Lithium diisopropylamide was prepared at -78° from dry diisopropylamine and n-butylithium 2.45M in hexane. Ethyl bromoacetate, iodomethane, 2-chloroethanol, and 2-iodoethanol were obtained from Aldrich Chemical Company and used without further purification. The degree of functionalization (DF) is the fraction of the original functional groups which has undergone chemical modification.

Poly(methyl acrylate) was prepared as follows: a 1L polymerization kettle fitted with a reflux condenser and a mechanical stirrer was charged with 200 ml of freshly boiled, distilled, water, 2g of sodium oleate, 1g of Adogen 464, 0.1g of ammonium persulfate and 99g of freshly distilled methyl acrylate. The mixture was stirred and its temperature was raised until the polymerization started. After 1 hour reflux, the polymer was collected, washed with water, then dissolved and precipitated to yield 82.6g of material with an intrinsic viscosity of 1.48 (acetone, 31). GPC data: Mn-320,000; Mw-670,000 (polydispersity, 2.09). Analysis: C, 55,74; H, 7.05; O, 37.41.

To a solution of 5g of the above polymer (1) cooled to 0° in 250 ml of dry THF was added a solution of lithium diisopropylamide prepared at -78° by adding 25 ml of 24.5M n-butylithium to 8.4 ml of diisopropylamine in 20 ml THF. After 1 hour at 0°, the polymeric enolate (2) was treated with an excess of electrophile. For example, polymer (2) was treated with 17g of ethyl bromoacetate and the mixture was stirred overnight at room temperature. After precipitation in a large amount of petroleum ether (30-60) the product was washed with water, redissolved in THF, dried, and reprecipitated from petroleum ether. After drying in vacuo, 4.1g of polymer (3) were obtained. Analysis of the polymer indicates a degree of functionalization of approximately 0.65. In addition, elemental analysis (0.96% N) is consistent with 5-6% amidation.

In a similar reaction, enolate (2) was quenched with excess powdered dry ice and the mixture was then treated with 40 ml HMPT and evaporated under reduced pressure to remove some of the solvents. The resulting solution was then treated at room temperature with 10 ml iodomethane. An exothermic reaction accompanied by much frothing of the polymer solution was observed following which the solution was stirred overnight. After precipitation in methanol, the polymer was washed, then dissolved, and reprecipitated. Analysis of (4) shows a degree of functionalization of 0.4. Incorporation of 0.75% N is consistent with less than 5% amidation.

Enolate (2) was also quenched by addition of excess liquid sulfur dioxide. The resulting solution was stirred at room temperature until most of the sulfur dioxide had evaporated, then (polymer (5)) treated with excess iodomethane, 2-chloroethanol, or 2-iodoethanol and heated overnight at 60°. After precipitation and reprecipitation the polymer was dried and analyzed. In a typical preparation, polymer (6) contained 11.8% sulfur and 2.24% nitrogen, correspond to a degree of functionalization of 0.55 and 23% amidation.

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