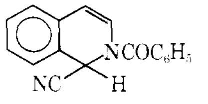
Communications to the Editor

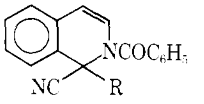
Chemical Modification of Polymers. III. An Unusually Facile Displacement Reaction Involving the Anion of a Reissert Compound

Our interest in the chemical modification of polymers[1,2] arises from the opportunity for altering in a controlled manner the physical and chemical characteristics of polymeric materials. Preparation of several structurally different polymers and copolymers from a given reactive polymer is also advantageous for some studies. In addition polymer modification reactions can be utilized to prepare materials difficult or impossible to prepare by polymerization either because of problems in the polymerization process itself or in synthesis of the requisite monomer. As part of our continuing studies of such transformations the present report is a description of an unusually facile polymer reaction proceeding in essentially quantitative yield and conversion.

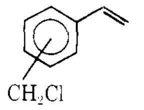
The utility of Reissert compound intermediates in synthesis of heterocyclic organic compounds is well documented.[3] For example 2-benzoyl-1,2-dihydroisoquinaldonitrile (I, an isoquinoline Reissert compound) when treated with base gives rise to the corresponding anion, which reacts quite readily with alkyl halides yielding 1-alkyl-2-benzoyl-1,2-dihydroisoquinaldonitriles (II).[4-7] The reactivity of these compounds and our prior interest in them prompted us to examine this alkylation reaction using a polymeric substrate.



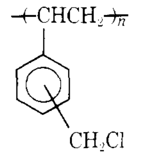
I



II



III

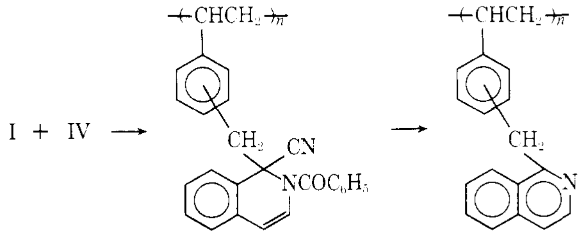


IV

Vinylbenzyl chloride (III), a 60–40 meta/para mixture (Dow Chemical Co.), was polymerized using a free radical imitator. The resultant polymer, poly(vinylbenzyl chloride) (IV), was precipitated from tetrahydrofuran (THF) solution by dropwise addition to methanol. Elemental analysis (Calcd for C_9H_9Cl: C, 70.82; H, 5.94; Cl, 23.23. Found: C, 70.89; H, 5.80; Cl, 23.12) supports the assigned structure. It had $\bar{M}_n$ 30.4 × 10^3 and $\bar{M}_w$ 64.1 × 10^3.

The polymer IV was employed to test the feasibility of the proposed grafting reaction. Reaction of 1.45 equiv of I *via* its anion with poly(vinylbenzyl chloride) (IV) at room temperature in dimethylformamide (DMF) using the method of Popp and Wefer[5] led to a quantitative yield of poly[1-(vinylbenzyl)-2-benzoyl-1,2-dihydroisoquinaldonitrile] (V). Elemental analysis (Calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.36; N, 7.44. Found: C, 82.81; H, 5.36; N, 7.35) indicates 100% conversion. The infrared spectrum contains the expected carbonyl band at 1695 cm^{-1}, which agrees well with that of monomeric analogs.[8] Its ultraviolet (uv) spectrum (λ_{max} 317, 300, 287 (sh) nm in THF) is similar to monomeric analogs such as II, R = $CH_2C_6H_5$ (λ_{max} 315, 298, 285 (sh) nm in THF). The molecular weight distribution of V is very similar to starting polymer IV and there is no evidence of degradation or cross-linking.

Alkaline hydrolysis of V led in quantitative conversion to poly[1-(vinylbenzyl)isoquinoline] (VI) (Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.61; H, 6.22; N, 5.68). Its infrared spectrum has no carbonyl peak. Its uv spectrum (λ_{max} 321, 308, and 272 nm in THF) also reveals structural changes relative to polymer V. Namely, the shift of the long wavelength absorptions to longer wavelength is consistent with aromatization of the isoquinoline nucleus.[9] The molecular weight distribution is relatively unchanged with no apparent cross-linking or degradation.



V VI

Both of the polymers V and VI are soluble in solvents such as THF, benzene, chloroform, and DMF and insoluble in water, methanol, and hexane. Thus, their solubility properties appear to be similar to polystyrene and poly(vinylbenzyl chloride).

The highly efficient conversion of poly(vinylbenzyl chloride) to V and VI thus demonstrates the feasibility of this chemical modification of reactive polymeric halides. In fact the results are surprisingly good on two counts. (1) First, the formation of V is cleaner and more efficient than usual monomer reactions involving benzyl halides. The Reissert compound I has been reacted with a number of substituted benzyl halides under these same reaction conditions and the yields of II (R = *p*-$CH_2C_6H_4$-X) vary from 65 to 84%.[7,9,10] The condensation with *p*-methylbenzyl chloride, which is a good molecular model for IV, proceeds in 78% yield.[10] In contrast to reactions of other primary alkyl halides the crude products from these monomeric benzyl halides are generally gummy. While this has not been investigated, the formation of carbenes by proton abstraction from the benzyl halide may lead to side reactions resulting in formation of gummy products. The high yield and conversion in the case of the polymeric benzyl chloride IV might then be a consequence of decreased formation of carbenes by virtue of the shielding effect of the "soft" hydrocarbon-like polymer environment, which inhibits approach of the relatively "harder"[11] base, hydride ion. (2) Second, chemical reactions of pendant groups on polymers tend in general to be sluggish (*e.g.*, ref 1) and complete conversion is difficult to achieve,[12] though in some cases satisfactory conversions are attainable.[13] The point made above concerning the effect of the hydrocarbon-like environment provided by the polymer backbone on reactivity in typical electrophilic and nucleophilic transformations may apply generally to vinyl polymers. In our previous work on aminolysis of poly(methacrylate esters) the lack of solvent effect on rate was taken as "an indication that the medium is made polar on a molecular basis by the DABCO (diazabicyclooctane, a catalyst) and thus polar solvents exert little additional effect."[1] In retrospect, the absence of a solvent effect is more completely rationalized in terms of the soft character of the immediate environment of the reaction site. In the present instance the anion of I is apparently a nucleophile of optimal softness so that it is able to readily approach the reactive function on the polymer. In summary then the high conversion is attributed to high selectivity for the desired reaction to the exclusion of side reactions on the basis of the relative hardness of the species attacking the polymer, which acts as its own local solvent medium.

Conclusions

Reaction of poly(vinylbenzyl chloride) and the anion of 2-benzoyl-1,2-dihydroisoquinaldonitrile proceeds smoothly and in quantitative conversion by displacement of chloride ion. The resultant polymer is readily hydrolyzed to afford a polymer bearing an isoquinoline ring system in quantitative conversion and good yield. This process provides a route to polymers difficult to obtain by direct polymerization.

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References and Notes

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