molecular origin of the empirical C_2 term in the Mooney–Rivlin equation.

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On the Anisotropy of Composite Networks

Recently the elastic behavior of some specially prepared polymer networks was reported by Kramer, *et al.*[1] These networks, cross-linked in states of strain just above the glass transition temperature, were analogous to composite networks[2] in that an entanglement structure provided a stress level during cross-linking; the entanglements served as first stage cross-links.

These networks, prepared from polybutadiene, were mechanically anisotropic, with a lower modulus along the initial direction of stretch than in the transverse direction. Such anisotropy is in the opposite sense to that previously reported for true composites of rubber,[3] where the modulus along the transverse direction is lower. The theory of composites, based on Gaussian chains, cannot account for such anisotropic behavior.[2,4–6]

We wish to point out, however, that composite theory derived from non-Gaussian statistics does predict anisotropic elastic behavior.[7,8] One such model,[8] a composite network composed of a most probable chain contour length distribution of non-Gaussian chains undergoing an affine deformation, is in qualitative agreement with the experimental results of Kramer, *et al.*[1] Therefore, to the extent that entanglement–cross-link composites are comparable to cross-link–cross-link composites, we view their data as being an experimental validation of our theoretical results.[8] Since the theoretical anisotropy arises from the use of the most probable contour length distribution, a monodisperse system being isotropic, it is suggested that chain length distributions can have important bearings on the mechanical behavior of elastomers. The data reported by Kramer, *et al.*,[1] tend to add substance to this conclusion.

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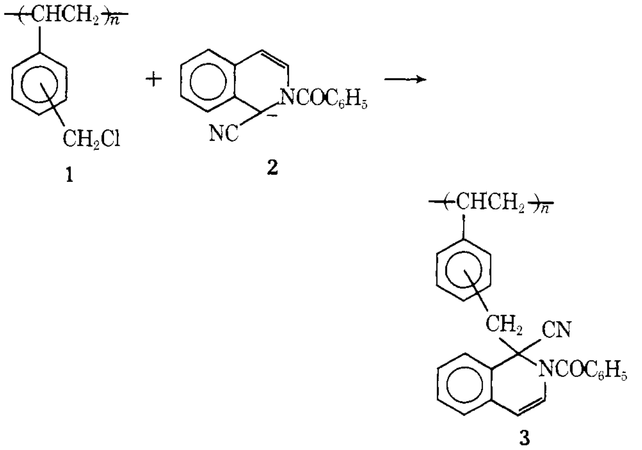
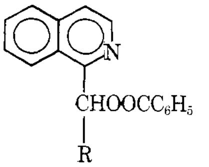
Chemical Modification of Polymers. IV. Another Example of Facile Nucleophilic Attack on a Polymer by a Reissert Anion

Recent progress in the field of chemical reactions of polymers[1,2] brought to our attention the opportunities for controlled alteration of chemical and physical properties of polymers. Our studies[3–5] have concentrated on polymeric reactions in solution. This allows more facile and complete analysis of the reaction process and products, while at the same time affording polymers of potentially greater utility than insoluble polymers.

In the previous report in this series the reaction of Reissert compounds and polymers bearing displacable halogens was examined and shown to be an excellent means of attaching aza-aromatic moieties to polymers.[5] Specifically, poly(vinylbenzyl chloride) (1) was reacted with the anion (2) of 2-benzoyl-1,2-dihydroisoquinaldonitrile. Displacement of chloride ion occurs, resulting in formation of poly[1-(vinylbenzyl)-2-benzoyl-1,2-dihydroisoquinaldonitrile] (3).



Other reactions of Reissert compounds[6] seem to be adaptable to grafting reactions of polymers. Among these is the reaction of aldehydes. The Reissert anion **2**, for instance, reacts with aldehydes (RCHO) to produce ester **4**



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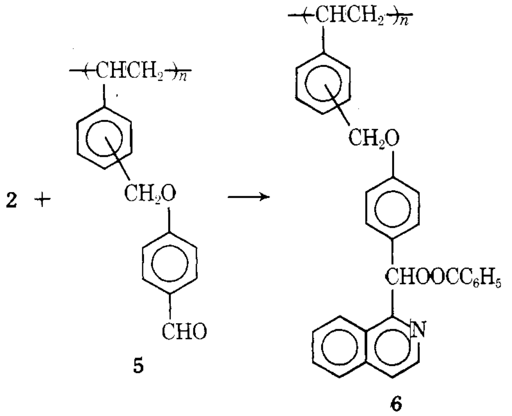
via an intramolecular rearrangement with loss of cyanide ion, resulting in aromatization.[7] This reaction proceeds with aliphatic aldehydes[7-9] as well as aromatic aldehydes.[7,10,11]

The present report describes the reaction of the anion of the isoquinoline Reissert compound **2** and a polymeric aldehyde as part of our synthetic efforts in this field.

The lack of commercially available polymeric aldehydes necessitates the synthesis of such polymers. For this purpose we utilized the reaction of poly(vinylbenzyl chloride) and phenols which we previously reported.[4] Polymer **1**[4,5] was reacted with *p*-hydroxybenzaldehyde in basic solution; poly[(4′-formylbenzyloxy)styrene] (**5**) resulted in 100% conversion.[4] Its infrared spectrum contains an intense carbonyl band at 1690 cm^{-1}. Its molecular weight distribution (MWD) (2.16) is very similiar to starting polymer 1 (2.11) as determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF). Both GPC and viscometry ($[\eta]$ = 0.21 and 0.20 dl/g for **1** and **5**, respectively, in THF at 25°) indicate the absence of cross-linking and degradation.

The reaction of the Reissert anion **2** and polymeric aldehyde **5** was carried out at 20° under nitrogen in dimethylformamide (DMF).[5] Poly[4-(vinylbenzyloxy)phenyl-1-isoquinolylcarbinyl benzoate] (**6**) was formed in approximately 100% conversion (after purification by several precipitations from THF solution by dropwise addition to hexane and 80% ethanol: *Anal.* Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97. Found: C, 80.85; H, 5.29, N, 2.91) and approximately 100% yield. Its infrared spectrum contains an intense band at 1715 cm^{-1} attributable to the ester carbonyl and shows no evidence of the aldehyde carbonyl band of **5** at 1690 cm^{-1}. The carbonyl band of model monomeric compound **4**, R = C_6H_5,[11] is at 1722 cm^{-1}. The MWD of **6** (2.38 in THF by GPC) is similiar to that of **5**. Thus, GPC as well as viscometry ($[\eta]$ = 0.19 dl/g in THF at 25°) indicate that side reactions leading to cross-linking or degradation are insignificant. Polymer **6** is soluble in THF, benzene, DMF, and chloroform, but insoluble in methanol, ethanol, water, and hexane.



The ultraviolet (uv) spectrum of polymeric ester **6** in THF contains peaks at 321, 309, and 273 nm. These peaks are characteristic of the 1-benzylisoquinoline moiety;[5,12] thus, their presence in the spectrum of **6** confirms the presence of this moiety.

The excellent conversion obtained in this grafting reaction is noteworthy in comparison to reactions of monomeric aldehydes. Only one reaction of the Reissert anion **2** and an aldehyde, namely benzaldehyde to yield **4**, R = C_6H_5, under these conditions (room temperature, DMF) has been reported and the crude yield was 65%.[13] *p*-Benzyloxybenzaldehyde and **2** lead to a 68% crude yield of the expected ester at −30° in ether–dioxane,[11] while benzaldehyde leads to an 88% yield.[7] In benzene at 80° the latter reaction proceeds in 79% yield.[11] The significance of the high conversion in the present polymeric system is even greater considering the generally sluggish nature of polymers in chemical reactions.[14] While the higher yield in the polymer system may in part be due to ease of isolation, it is believed that the local environment of the reactive center provided by polymer itself enhances the rate of the desired reaction relative to side reactions as previously suggested.[5]

Thus, as in the previous example,[5] the reaction of the Reissert anion **2** with a polymeric substrate proceeds in higher yield than with corresponding monomeric substrates. Morever, the virtually complete conversion is unusual for a reaction on a polymer. Although in this case the reaction moiety is at an appreciable distance from the backbone, another sytrene polymer bearing a formyl group on the phenyl ring also reacts to nearly complete conversion. This process, the hydrolysis of polymeric ester **6**, and detailed spectroscopic data will be described in the full paper as we continue to explore these facile chemical modifications of polymers.

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Domain Morphology of Star Block Copolymers of Polystyrene and Polyisoprene

The morphology of linear polystyrene–polydiene block copolymers has received intensive scrutiny over the past several years *via* the application of electron microscopy[1-13] and small-angle X-ray scattering.[14-16] Electron micrographs of these block copolymers show that there is a pronounced tendency for polystyrene (when it is the minority component) to form ordered domains in the polydiene matrix. Small-angle X-ray scattering has also clearly shown the lattice-like arrangement of the polystyrene domains.

The most commonly examined materials have been linear di- and triblock copolymers where the polystyrene content has ranged between 10 and 40 wt %. Contrasting interpretations have been made as to the structure of the phase-