[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Copolymerization of 1,3-Butadiene with Some Polynuclear Aromatic Hydrocarbons[1]

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A number of aromatic hydrocarbons have been tested as comonomers for copolymerization with 1,3-butadiene. Anthracene, pyrene and *trans*-stilbene form copolymers having marked ultraviolet absorption. Under similar conditions benzene, naphthalene, phenanthrene and *cis*-stilbene do not give copolymers with detectable absorption maxima. The reactivities of these aromatic compounds fall in an order predicted from their free valence numbers as calculated by the molecular orbital method. These calculations predict high reactivity for several as yet untested polynuclear systems.

During the course of a search for some new monomers for copolymerization with 1,3-butadiene it has been found that *trans*-stilbene and pyrene will yield copolymers and their ultraviolet absorption spectra have been obtained. Conditions for the preparation were approximately those used on an industrial scale for the emulsion copolymerizations of styrene and butadiene.

As expected from the low reactivity of benzene in copolymerization reported by Stockmayer and Peebles[2] no special evidence could be obtained for copolymerization of benzene and 1,3-butadiene.[3] The butadiene polymer prepared in the presence of naphthalene shows none of the absorption maxima of a 1,4-dialkyl-1,4-dihydronaphthalene. Butadiene in the presence of phenanthrene likewise yields polymers without aromatic absorption. It may be calculated that 0.01% of phenanthrene incorporated by reaction at the 9,10-bond should be readily detected through the absorption of the diphenyl unit in the copolymer. It might have been anticipated that the double-bond character of the phenanthrene 9,10-bond would lead to copolymerizability; however the molecular orbital calculations predict equal reactivity for phenanthrene and naphthalene.[4] When butadiene is polymerized in the presence of phenanthrene which is not sufficiently pure, the polymers have marked absorption maxima in the 2000–3000 Å. range. This absorption may be traced to the presence of anthracene and fluorene incorporated by copolymerization and chain transfer, respectively. Magat and Bonême[5] noted that the thermal polymerization of styrene was sharply retarded by phenanthrene. Their sample of phenanthrene was not subjected to purification, however, and probably contained anthracene as an impurity.[6] Polymerization of butadiene in the presence of fluorene yields relatively low molecular weight polymers having the absorption spectrum of a 9-alkylfluorene. The generally accepted mechanism of chain transfer by α-methylene groups is thus substantiated. The large chain transfer constant[7] and large extinction coefficient of fluorene[8] combine to make the fluorene end-groups detectable.

The high reactivity of anthracene has been reported previously[3] and is now interpreted as the result of the high free valence at the *meso* positions.

trans-Stilbene was found to be less reactive than anthracene in accord with the prediction based on free valence calculation.[4] *cis*-Stilbene is considerably less reactive toward butadiene than the *trans*-isomer. The lower reactivity of *cis*-stilbene in copolymerization has been explained by Lewis and Mayo[9] in terms of a high-energy, sterically unfavorable transition state for copolymerization of the *cis*-isomer.

Spectral evidence for the copolymerization of pyrene also has been obtained. Maximum free valence occurs at positions 1, 3, 6 and 8[10] and copolymerization may therefore be expected to yield a copolymer containing a mixture of 1,6-dialkyl-1,6-dihydropyrene and 1,8-dialkyl-1,8-dihydropyrene units where the "alkyl" group is the polybutadiene chain. The ultraviolet absorption spectra of the model compounds 1,6-dihydropyrene and 1,8-dihydropyrene have not been recorded and consequently the copolymer composition and structure cannot be determined with certainty at this time.

It now seems possible to predict high copolymerization reactivity for a number of the higher polynuclear hydrocarbons. For example, if suitable reaction media can be found, vinyl copolymers containing large proportions of naphthacene or 1,2-benzpyrene can undoubtedly be prepared. A correlation between susceptibility to free radical attack and free valence number has been noted before,[5,11] and it is to be expected that reactivity in copolymerization should parallel that in other free radical reactions.

Experimental

Copolymerizations were conducted in emulsion at 50° in four-ounce screw-cap bottles sealed with rubber gaskets. But for the one exception mentioned below, each charge contained 30 ml. of a 2.86% solution of soap (OSR specification L.M.2.3.0.5.2.), 0.025 g. of technical lauryl mercaptan and 2.0 ml. of a 3.0% solution of potassium persulfate in addition to monomers and solvent. After tumbling end-over-end in a constant temperature bath, the product was isolated by the addition of 10 ml. of a 4% solution of sil-

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furic acid saturated with sodium chloride. Purification was accomplished by washing with water and repeatedly precipitating the polymer from carbon disulfide solution by adding the copolymer solutions to acetone. Copolymer absorption spectra were obtained with a Cary recording spectrophotometer, Model 11, using solutions in tetrahydrofuran. The solvent was purified by distillation from calcium hydride and was used immediately thereafter. Peroxides present in solvent which has not been freshly distilled cause gelation of butadiene copolymers.

Naphthalene.—Technical naphthalene was recrystallized from ethanol and sublimed. A monomer and solvent charge consisting of 2.0 g. of naphthalene, 5.0 ml. of benzene and 8.0 g. of butadiene was employed. After tumbling for 15.75 hours a 63% conversion was obtained. After four precipitations the copolymer exhibited no absorption maxima in the range 2300–4000 Å. (concentration 17 g. per liter).

Phenanthrene.—Phenanthrene was purified by repeated distillation from sodium,[12] treatment with maleic anhydride and refluxing benzene,[13] subsequent extraction with 10% sodium hydroxide and crystallization from ethanol. A charge containing 10 ml. of benzene, 2.0 g. of phenanthrene and 8.0 g. of butadiene in the usual medium was tumbled 13 hours to yield a copolymer in 41% conversion. The purified copolymer exhibited no absorption maxima in the range 2300–4000 Å. (concentration 6.1 g. per liter). Similar results were obtained using a sample of synthetic phenanthrene.

Fluorene.—A charge consisting of 35 ml. of soap solution, 2.0 ml. of potassium persulfate solution, 0.050 g. of mercaptan, 10.0 ml. of benzene, 2.0 g. of fluorene (m.p. 112–113°) and 18.0 g. of butadiene yielded a polymer in 28% conversion after tumbling for 12.75 hours. After six precipitations the polymer showed absorption maxima at 3025, 2910, 2665, 2640 and 2580 Å. Four more precipitations produced no further change in the intensity of these maxima. Fluorene must therefore be chemically incorporated in the polymer. The spectrum of 9-methylfluorene[8] agrees well with that of the polymer.

***trans*-Stilbene.**—Eastman Kodak Company white label *trans*-stilbene was recrystallized from ethanol before use. The usual amounts of emulsifier, initiator and modifier, 10 ml. of benzene, 1.0 g. of *trans*-stilbene and 9.0 g. of butadiene were tumbled for 11 hours to yield a copolymer in 40% conversion having absorption maxima at 2690, 2590 and 2530 Å. (concentration 15 g. per liter). Bibenzyl exhibits absorption maxima at 2695, 2645, 2620, 2590, 2540 and 2490 Å. Repetition of the copolymerization with the *trans*-stilbene charge increased to 2.0 g. and butadiene decreased to 8.0 g. gave a copolymer having maxima at 2690, 2655, 2620, 2590, 2540 and 2480 Å. (concentration 16 g. per liter). After correction for the absorption due to polybutadiene the stilbene content of the copolymer prepared from the 20% stilbene charge was calculated from the extinction coefficient of bibenzyl and found to be about 1%.

***cis*-Stilbene.**—This monomer was prepared by the method of "Organic Syntheses."[14] One gram of *cis*-stilbene, 10 ml. of benzene, 9.0 g. of butadiene in the previously described emulsion yielded a product in 41% conversion after tumbling for 11 hours. No absorption maxima were noted in the range 2300–4000 Å. (concentration 15 g. per liter).

Pyrene.—Thirty-five grams of the "pure" grade of pyrene from the Gesellschaft für Teerverwertung was refluxed in 400 ml. of toluene with 5 g. of maleic anhydride for four days. To the toluene solution was added 150 ml. of 5% potassium hydroxide and the mixture was refluxed for five hours with occasional shaking. After the aqueous layer was rejected, the toluene layer was thoroughly washed with water, concentrated to about 100 ml. and allowed to cool. The crystals of pyrene were removed by filtration and recrystallized twice from ethanol to give light yellow crystals, m.p. 148.5–149.5°, having an ultraviolet spectrum in good agreement with that given by Clar[15] for pyrene free of anthracene derivatives.

Copolymers were prepared from a charge containing 10 ml. of benzene, 1.0 g. of pyrene and 9.0 g. of butadiene in the previously described recipe. After seven precipitations the copolymer exhibited absorption maxima at 3420, 3015 and 2600 Å. It is to be noted that these absorptions do not rule out 4,5-attack since 4,5-dihydropyrene has been found to absorb at nearly the same wave lengths.[16]

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The Synthesis of Indone and Some Related Compounds[1]

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An improved synthesis of indone has been described and this ketone has been further characterized. Some intermediates and derivatives have also been reported. Indone homopolymerized with extreme ease under a variety of conditions but copolymers with butadiene were not obtained.

Indone (I), a cyclic α,β-unsaturated ketone, was desired in order that it might be compared with benzalacetophenone[2] as a comonomer in butadiene polymerization. The literature contains one account by Stoermer and Asbrand[3] of its preparation in low yields from the condensation of indene and *p*-nitrosodimethylaniline followed by hydrolysis. We have found that indone can be prepared in fair yields from indanone (II) by conversion to 2-acetoxyindanone (III) with subsequent elimination of acetic acid. It has also been prepared by the dehydrobromination of 3-bromoindanone (IV) with *sym*-collidine and by the debromination of 2,3-dibromoindanone with sodium iodide, but these do not seem to be satisfactory synthetic reactions because of the difficulty of obtaining these bromo compounds.

Indone is a light yellow oil which polymerized with extreme ease at ordinary temperatures even in diffused light. It is a powerful vesicant and lachrymator. Inhibitors such as hydroquinone, copper, copper salts and *t*-butylcatechol would not keep it from polymerizing. Trinitrobenzene would prevent polymerization if the ketone was stored at

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