tion of the viscoelastic behavior of entangled polymer systems.

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Poly(2-vinylfluorenone). II. Synthesis and Photochemistry of a Diazofluorene-Containing Polymer

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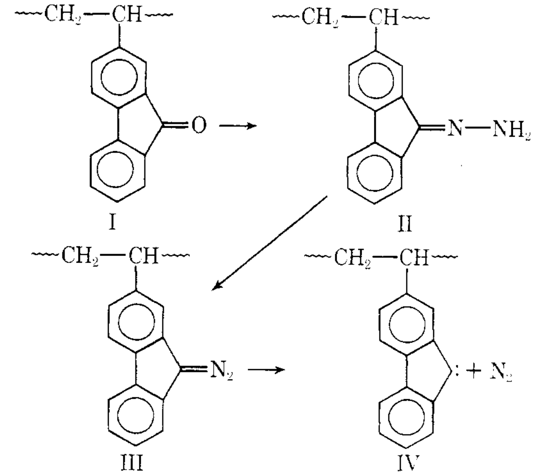
Photosensitive polymers are widely used in a number of important industrial technologies. Most of these utilize the difference in solubility, resulting from crosslinking reactions induced by light of the appropriate wavelength, in light and dark areas to create relief images which are further processed, *e.g.*, by photoresist techniques. The recent literature describes a number of interesting polymeric materials containing cinnamate,[1] acetylenic,[2] cyclopropene,[3] azido, and sulfonylazido[4] functions, and several comprehensive reviews[5,6] have appeared.

With few exceptions, the chemistry in these systems involves coupling processes leading to crosslinked, insoluble materials, *e.g.*, the photocyclodimerization of cinnamate groups and the formation and reactions of highly reactive radical fragments (nitrenes) produced in the photodissociation of azides. More recent efforts have been directed toward increased speeds and higher sensitivity through synthetic modification and improved sensitizers.

This note describes the synthesis of a novel photosensitive polymer containing diazofluorene groups. Photolysis of aryl and diaryldiazo compounds in solution has been reported[7] to give the corresponding carbene and nitrogen with high quantum efficiency ($\phi \sim 0.7$ to 0.9). Carbenes, or divalent carbon intermediates, are highly reactive species which undergo a wide range of addition, abstraction, and insertion reactions as well as coupling reactions.[8] The products from many of these highly nonselective processes are free radical in nature and these can react further by conventional radical reactions. A wide variety of crosslinking possibilities can be readily recognized if such entities could be introduced into a polymer material. Polymers possessing diazo groups have not been reported, probably due to the pronounced thermal instability of such compounds. Diazo compounds are, however, claimed[9] to be extremely efficient photocrosslinking agents for certain polymers.

The synthesis of 2-vinylfluorenone has made polymers and copolymers containing fluorenone groups (I) a reality.[10] 9-Fluorenone can be readily converted into 9-diazofluorenone and this diazo compound has a melting point of 94–95° and good thermal stability. Polymers containing diazofluorene groups have been prepared from 2-vinylfluorenone polymers by conversion to the hydrazone and subsequent oxidation. Treatment of the homopolymer of 2-vinylfluorenone or copolymers of 2-vinylfluorenone, *e.g.*, with styrene, in pyridine at 50° with hydrazine gave the corresponding hydrazone (II)-containing polymer which was isolated and purified. The conversion was best controlled by varying the concentration of hydrazine and the reaction time. At temperatures above 50° polymer insolubility became a severe problem. The use of excess hydrazine resulted both in conversion of fluorenone to fluorene groups (the result of an unusually facile Wolff–Kishner rearrangement) and insoluble products. The hydrazone-containing polymers were characterized by ir analysis. Oxidation of the hydrazone groups in the polymers to diazofluorene (III) groups was most effectively carried out at ambient temperatures using silver oxide. The hydrazone polymer was dissolved in a 90:10 THF/Et$_2$O mixture and freshly prepared silver oxide, and a few drops of alcoholic KOH were introduced and the reaction mixture stirred for 15–30 min. The polymer was isolated by precipitation into a nonsolvent. Longer reaction times and higher temperatures gave insoluble products. On the basis of small molecule control experiments the conversion of hydrazone to diazofluorene was assumed to be nearly quantitative under the experimental conditions employed. The polymers were yellow/orange/red in color, depending on the concentration of diazo groups. The ir spectra of poly(2-vinylfluorenone) and a polymer containing 5–10 mol % of diazofluorene groups are shown in Figure 1, top and bottom, respectively. The characteristic diazo band at 2060 cm^{-1} is evident. The reaction sequences shown were carried out on poly(2-vinylfluorenones) and on a styrene/2-vinylfluorenone (90:10) copolymer. The conversion of fluorenone to hydrazone and hydrazone to diazofluorene could be controlled by varying the reaction times using the prescribed experimental conditions. In general, polymers containing only a few mole per cent of diazofluorene groups were prepared and investigated, although a 50/50 copolymer of 2-vinylfluorenone/2-vinyl-9-diazofluorene was successfully isolated.



Although diazofluorene is apparently stable at ambient temperatures in the dark, polymers containing this functional group rapidly (within several days) became insoluble on storage in bulk or in solution. Storage at temperatures below 0° increased the functional lifetime of the material but such a limitation clearly precludes their practical utility. Apparently the thermal decomposition of diazofluorene

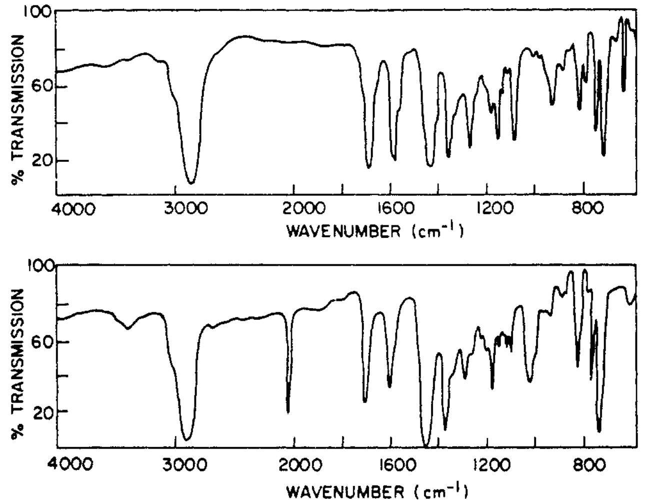


Figure 1. Ir spectrum of: (top) poly(2-vinylfluorenone) and (bottom) a copolymer of 2-vinylfluorenone:2-vinyl-9-diazofluorene.

groups in a polymeric environment leads to facile and efficient crosslinking and insolubilization. A control experiment with polystyrene containing 9-diazofluorene (2 mol % as in the test styrene copolymer) confirmed the efficiency of the crosslinking reactions.

Because of the thermal instability of the diazofluorene-containing polymers, the photocrosslinking reactions were not pursued in any detail and no sensitization experiments were made. Exposure of polymer films and polymer solutions to light of 3650 Å caused rapid insolubilization. The decrease in the intensity of the diazo band at 2060 cm^{-1} followed simple first-order kinetics and the quantum yield for carbene formation was estimated by conventional techniques to be in the range 0.6 to 0.9. Any attempt to define the mechanism of the reactions of the polymeric carbene (IV) would be highly speculative. Carbenes are known to undergo a wide range of abstraction, addition, coupling, and insertion reactions and most of these processes lead to free radical products, *e.g.*, $>\text{C:} + \text{RH} \rightarrow >\text{CH}\cdot + \text{R}\cdot$, which can participate in further abstraction, addition, and coupling reactions. Since each carbene, therefore, has the potential of generating more than one crosslink the overall photocrosslinking efficiency of such systems can be high.

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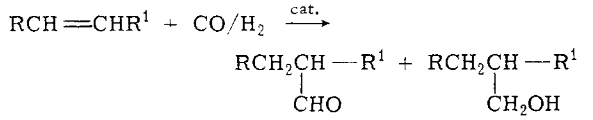
Communications to the Editor

Hydroformylation of a Polypentenamer and Preparation of Derivatives Therefrom

The oxo reaction for the conversion of olefins to aldehydes by the use of carbon monoxide and hydrogen, according to eq 1, has been known for a long time and is of considerable industrial importance in the manufacture of oxo alcohols.



$$\text{RCH}{=}\text{CHR}^1 + \text{CO/H}_2 \xrightarrow{\text{cat.}} \underset{\text{CHO}}{\text{RCH}_2\text{CH}}{-}\text{R}^1 + \underset{\text{CH}_2\text{OH}}{\text{RCH}_2\text{CH}}{-}\text{R}^1 \quad (1)$$

However, the hydroformylation of unsaturated polymers by this technique has apparently been largely neglected.[1] The reasons for this are most likely because of the instability of the product, cross-linking occurring due to reactions of the aldehyde side groups, and probable main chain degradation during the course of the reaction. These difficulties stem in large measure from the fact that with the "traditional" catalyst, dicobalt octacarbonyl, it is necessary to employ high temperatures and pressures in order to obtain reasonable conversions in fairly short times. Thus, a typical set of conditions for the hydroformylation of polybutadiene are reported as a gas pressure of 2400 psi (H_2:CO = 1:1), a temperature of 145°, and a reaction time of 3 hr.[1]

More recently there has been considerable interest in rhodium complexes as hydroformylation catalysts. Many of the details of these reactions have been elucidated by Wilkinson and coworkers.[2-4] These rhodium complexes are effective under much milder conditions than the cobalt complexes. This report represents the first application of these complexes to the hydroformylation of olefinic polymers, in this case a polypentenamer. It has been possible to incorporate up to 20 mol % of formyl side groups into the starting polypentenamer without cross-linking or main chain degradation, using the rhodium catalyst. In addition, it has been possible to convert the formyl side groups of the modified polypentenamer to the aldoxime and thence to the nitrile derivatives. Also hydrogenation has been carried out to convert the amorphous, unsaturated nitrile derivative to the crystalline, saturated polymer. The reaction sequence may be schematically represented as follows

$$\text{PP} \xrightarrow[\text{RhH(CO)(PPh}_3)_3]{\text{CO/H}_2} \text{PP-CHO} \xrightarrow[\text{pyridine}]{\text{HONH}_2\text{HCl}} \text{PP}{-}\text{CH}{=}\text{N}{-}\text{OH} \xrightarrow[\text{or P}_2\text{O}_5]{\text{Ac}_2\text{O}} \text{PP-CN} \xrightarrow[\text{TSH}]{\text{TPBSH}} \text{Hy-PP-CN} \quad (2)$$

where PP = starting polypentenamer, PP-CHO = polypentenamer derivative with formyl side groups, PP—CH=NOH = polypentenamer derivative with aldoxime side groups, PP-CN = polypentenamer derivative with nitrile side groups, TPBSH = 2,4,6-triisopropylbenzenesulfonyl hydrazide, TSH = *p*-toluenesulfonyl hydrazide, Hy-PP-CN = hydrogenated polypentenamer derivative with nitrile side groups.

Direct oxidation of the formyl group and hydrolysis of the nitrile group to the carboxylic acid has also been carried out and will be reported subsequently.[5]