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STUDIES ON AND WITH FUNCTIONALIZED POLYSTYRENES

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ABSTRACT

A number of useful functionalized polystyrenes have been prepared. Studies on fluoroalkyl ketone, fluoroalkyl carbinol, and hydroxy-contain polystyrenes, as well as polystyryl pyridine-based polymers, in regard to a variety of properties were made. These are discussed individually in regard to their reactions with alcohols to form hemiketals, miscibilization by hydrogen bonding, improvements in the thermostability of blends, and char formation at elevated temperature, respectively. In addition, enhancements of polystyrene and copolymers of modified polymers in regard to the oxidative stabilization of blends are discussed.

I. INTRODUCTION

It is possible to functionalize polystyrene and obtain interesting, potentially useful properties. Our research has shown that fluoroalkyl ketone-substituted polystyrenes have potential for the separation of mixtures of alcohols as well as the separation of alcohols from ketone-containing analogs [1–5]. Fluoroalkyl carbinol-containing polystyrenes are among the best hydrogen bond donating systems, and they are excellent miscibilizers with hydrogen bond-accepting polymers [6–10]. In miscible blends of poly(styrene) and hydroxy-substituted poly(styrene) with

poly(vinyl methyl ether), enhanced thermooxidative stabilization was observed [12, 13]. The thermal stability of poly(4-hydroxystyrene) was improved in the presence of a hydrogen-bond-accepting polymer [14]. When the polystyryl pyridine unit was incorporated into the backbone of a polymer enhanced char formation was shown, and a mechanism involving simultaneous crosslinking and ring formation was proposed [15-18].

II. FLUOROALKYLKETONE-CONTAINING POLYSTYRENES

Poly(*p*-vinyltrifluoroacetophenone) (PVTFA), prepared by free radical polymerization, had lateral order and crystallinity as demonstrated by DSC and X-ray studies [1]. Polymers of similar structure, such as poly(*p*-vinyl difluoroacetophenone) and poly(*p*-vinylphenylheptafluoropropyl ketone), did not show this crystallinity, and all the polymers including PVTFA were atactic according to 220-MHz proton NMR studies [2].

Fluoroalkyl ketone-based polystyrenes have the potential to separate mixtures containing various alcohols based on their equilibrium with their respective hemiketals [5]. The equilibrium constants are much more favorable for hemiketal formation when a methylene unit is inserted between the para-position and the trifluoromethylketo functionality.

Thus $p\text{-CH}_2\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-CF}_3$ was more efficient than $p\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-CF}_3$ by an order of magnitude [3]. By looking at the equilibrium constants for hemiketal formation, it was demonstrated that the efficiency of hemiketal formation with alcohols was methanol > ethanol > 1-butanol > benzyl alcohol > 2-propanol > cyclohexanol > *t*-butyl alcohol [3]. These differences were sufficient to conclude that the $\text{-CH}_2\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-CF}_3$ substituted styrenes could be used to design resins for the separation of mixtures of alcohols [3, 5].

III. HYDROXYL-CONTAINING POLYSTYRENES

A. Fluoroalkyl Carbinol-Modified Polystyrenes

We have been studying substituted hydroxyl groups which have strong hydrogen-bond-donating functionality from the viewpoint of miscibilization phenomena with hydrogen-bond-accepting polymers. Initially,

the para-substituted fluoroalkyl carbinol, $-\text{C}(\text{OH})(\text{H})\text{CF}_3$, was prepared by reduction of the trifluoromethyl ketone polymers with lithium aluminum hydride [6, 7]. This fluoro-alkyl carbinol was surprisingly good for miscibilizing a number of H-bond accepting polymers as judged by single T_g phenomena. Subsequently, *p*-hexafluoroisopropanol-substituted polystyrenes were prepared either by copolymerization of the monomer with styrene or by postreaction on polystyrene and were shown to be even more efficient for miscibilization [7, 8].

Miscibilization of a crystalline polymer, poly(ethylene oxide), was obtainable when sufficient fluoroalkyl carbinol was present to overcome crystallization forces [7]. The hydrogen bonding interactions were shown to be thermally reversible by FT-IR studies. Thus, hydrogen bonding decreased with elevated temperature, but reformed on cooling [7].

Miscibilization by hydrogen bonding was obtained with a variety of hydrogen bonding systems. The acceptor efficiency, and therefore the amount of H-bond donation required from the hexafluoroisopropanol-substituted polystyrene copolymer for miscibility, depended on the particular functionality, the crystallinity, and the stiffness of the accepting polymer [8]. The efficiency of such interactions could be calculated from the enthalpy of hydrogen bond formation determined from the magnitude of the hydrogen-bonded frequency shifts for the hydroxyl group (bonded vs unbounded) for the hexafluorocarbinol-substituted copolymers. For example, ΔH values varied from -5.3 kcal/mol with a poly(phenylene oxide) to -8.0 kcal/mol for poly(vinyl methyl ether) [8].

In the case where crystallinity was a major factor limiting miscibility, such as nylon 6,12, miscibility was achieved by systematically destroying the crystallinity by *N*-alkylation [10].

B. *p*-Hydroxyl Modified Polystyrenes

1. Miscibilization

Copolymers of styrene and *p*-vinylphenol were shown to miscibilize hydrogen-bond-accepting polymers [7]. The effect of steric factors on the accepting polymer were evaluated on the basis of comparing miscibility in *n*-butyl acrylate and *t*-butyl acrylate copolymers. Poly(*t*-butyl acrylate) was immiscible with poly(4-hydroxystyrene), whereas poly(*n*-butyl acrylate) was miscible. Miscible blends were obtainable when the *n*-butyl acrylate content of the copolymer with *t*-butyl acrylate was 64% or higher. A miscibility window was found for poly(*t*-butyl acrylate) with

poly(styrene-*co*-4-hydroxystyrene) when the amount of 4-hydroxystyrene in the copolymer was between 28 and 66 mol%.

IV. THE THERMAL AND OXIDATIVE STABILITY OF POLYMERS CONTAINING HYDROXYL-MODIFIED POLYSTYRENES

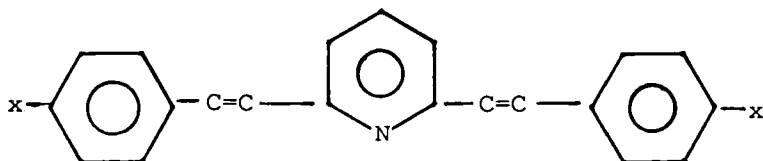
We have shown that poly(styrene) (PS) in miscible blends with poly(vinyl methyl ether) (PVME) prolongs the induction period of PMVE oxidation [12]. This effect appears to be related to miscibilization since very low molecular weight PS extends the induction period, and after long induction periods, when phase separation occurred, the oxidation rates returned to normal [12].

Hydrogen bonding from modified polystyrenes with small amounts of hydroxyl modification (1–2 mol%) should increase miscibility and, therefore, induction periods for PVME oxidation. This indeed was the case for both hexafluoroisopropanol and hydroxy-modified styrene copolymers [13, 14]. The latter was more efficient than the former in prolonging the induction, and it was explained on the basis that the 4-hydroxystyrene-containing copolymers could also function as antioxidants [13].

In studies on blends of poly(4-hydroxystyrene) with polymers such as poly(vinyl pyrrolidone) and poly(ethyl oxazoline), the thermal stability of poly(4-hydroxystyrene) improved [15]. The initial degradation of poly(4-hydroxystyrene) appeared to be by the formation of ether groups. Complexation of the hydroxyl group, in this case with polymers, apparently altered the ability to form ether groups and accounted for, in large part, the increase in thermostability. The weight loss of poly(4-hydroxystyrene) was about 6% in the temperature range 200–250°C, and no weight loss was observed in this range for the polymer blends.

V. POLY(STYRYLPYRIDINES)

Poly(styrylpyridines) was prepared by the reaction of methyl-substituted pyridines with the appropriate aldehydes. By the reaction of such aldehydes with 2,6-dimethyl pyridine, we prepared dihydroxy-dicarboxyl and diamine-containing intermediates,



where x is hydroxyl, amino, or carboxyl acid groups, useful in preparing epoxy resins [16], polyesters [17], polyamides [18, 19], and polyurethethanes [18, 19]. These polymers give a high char residue at elevated temperatures. High char-forming polymer systems have potential use for systems with reduced flammability. A proposed mechanism for this increased char formation is an interchain Diels-Alder addition which generates simultaneous crosslinking and ring formation, followed by a Claisen rearrangement to give a thermally stable polymer which could not undergo a retro-Diels-Alder reaction [17]. The series of linear polyesters prepared from 2,6-bis(*p*-hydroxystyryl) pyridine and terephthalic acid, isophthalic acid, adipic acid, and sebacic acid was thermally stable in the 365 to 450°C range, and, as expected, the decomposition temperatures were higher for the aromatic polyesters and lower for their aliphatic analogs [18, 19]. Similar observations were noted for the polyamide series [18]. All aromatic polyimides prepared from the diamine showed the highest heat resistance with little decomposition at 450°C, while the polyurethanes had the least heat resistance [18].

These polymers were also photoreactive, participating in a 2 + 2 cycloaddition reaction [17, 18]. Protonated complexes of polyesters with trifluoroacetic acid absorbed at longer wavelengths and were also photoreactive [18]. Unfortunately, in all cases the photoreactivities had low quantum efficiencies.

VI. CONCLUSION

Modification of the poly(styrene) structure continues to lead to interesting functionalized polymers having a wide spectrum of properties. The observations reported led to further functionalization research which extended concepts related to areas such as separation processes, blend miscibilization, polymer stabilization, and reduced flammability.

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