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Radiation and UV Grafting of Monomers to Polyolefins and Cellulose Acetate. Significance of These Studies in Reagent Insolubilization Reactions

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ABSTRACT

In the simultaneous irradiation procedure, sensitized UV radiation is shown to be a complementary initiator to ionizing radiation for the grafting of monomers to polyolefins. Parameters influencing the yield of graft have been considered, including the role of sensitizer, solvent, and the type of monomer. These results indicate why difficulties have been experienced by previous authors in photografting monomers to polymers using analogous procedures. Grafting of styrene to cellulose acetate using ionizing radiation at low total doses is also reported. Difficulties associated with the poor grafting yield to gel beads as opposed to films are considered predominantly in terms of moisture content and swelling of the gel beads. The feasibility of using the polyolefins and cellulose acetate beads modified by the present grafting methods in reagent insolubilization reactions is discussed.

INTRODUCTION

Extensive work involving the gamma-radiation-induced grafting of monomers such as styrene to polyolefins has already been reported [1-7]. Where a substituted styrene containing an appropriate group is used, it is possible to produce copolymers to which an enzyme or a catalytically active homogeneous metal complex may be attached. This is achieved by conventional chemical reactions involving the styrene substituent group. As an example, p-nitrostyrene is grafted to polypropylene and the nitro group in the resulting polymer reduced to the amine, to which is attached the catalytically active species [8]. Naturally occurring polymers such as cellulose [9] and wool [10] have also been modified to advantage in this manner by radiation copolymerization, and work in this area is now being extended to acetylated cellulose.

Previous reports on cellulose acetate have covered styrene grafting by simultaneous [11, 12] and pre-irradiation [12] techniques at dose levels mostly in excess of 1-2 Mrd (and up to 14 Mrd). In work reported here it was considered desirable to reduce these irradiation doses since these studies are being extended to the grafting of styrenes to cellulose acetate in the form of porous gel beads [13] for subsequent enzyme attachment. For this purpose the simultaneous radiation copolymerization procedure is the most suitable since surface, as distinct from bulk, copolymerization should result in a more efficient immobilization process.

One essential difficulty, however, with the gamma ray procedure is that certain monomers, such as substituted styrenes, may not graft with high efficiency. Where the functional group is deactivating, such monomers usually require radiation doses in excess of 2 Mrd to achieve grafting of around 10%. In addition, certain trunk polymers such as the polyolefins are susceptible to significant radiation degradation at doses above 2 Mrd. For these reasons replacement of gamma ray with UV irradiation to initiate grafting of monomers to polyolefins has been investigated.

With polyolefin trunk polymers, previous authors [14] have reported difficulty in the UV grafting of monomers such as acrylonitrile by the simultaneous irradiation method using a dye as sensitizer. More recently a method was developed by Tazuke and Kimura [15], using benzophenone (BPO) sensitizer dissolved in monomer solution, for the surface grafting of acrylamide, N-vinylpyrrolidone, and methacrylic acid to polyolefin films. However, yields were so low by this technique that analysis by gravimetric methods was not possible. Reasonable grafting yields of several monomers to polyolefins were achieved by Oster and co-workers [16] by incorporating the sensitizer, benzophenone, into the trunk polymer prior to irradiation. For practical reasons this technique possesses limitations since the films must be specially prepared; ordinary commercial polymer films need to be modified prior to irradiation, and the resulting grafted films contain significant residual amounts of sensitizer.

In this present paper, studies involving the simultaneous UV irradiation procedure are reported where the sensitizer dissolved in monomer solution is used for photosensitized copolymerization of styrene, 4-vinylpyridine, and methyl methacrylate to polypropylene and polyethylene. Furthermore, preliminary results are reported for styrene grafting to cellulose acetate using low dose gamma irradiation. These results are discussed in terms of the feasibility of immobilizing enzymes to cellulose acetate gel beads using this grafting technique.

EXPERIMENTAL

Styrene monomer (Monsanto Chemicals Ltd.) was freed from inhibitor by chromatography on activated alumina. Polypropylene (Shell) was isotactic, doubly oriented film (2.5 × 3.75 × 0.005 cm) and contained only calcium stearate (0.1%) and an antioxidant (0.1%). Cellulose acetate (powder, acetic acid content, 58%) was recrystallized from an acetone solution and dried under vacuum. Films (20 × 20 × 0.009 cm) were cast by application of a solution in acetone (20% w/v) to glass plates using a TLC layer applicator. After 2 h the films were peeled from the plates, cut into strips (1.5 × 4.5 cm), and dried under vacuum for 48 h. Commercially prepared cellulose acetate gel beads (CSR Chemicals) were washed exhaustively with dry ethanol to displace the water prior to irradiation. All solvents were AR grade and used without further purification.

UV Irradiation

Irradiations were performed in stoppered Pyrex tubes (25 mL), solvent being added first followed by photosensitizer and monomer to make a total volume of 20 mL. The trunk polymer was added to the grafting solution and the tube irradiated at a distance of 30 cm from a high pressure mercury 90-W (Philips) lamp (uranyl oxalate actinometer, using $\phi = 0.57$, gave 6.3×10^{-8} einstein/cm^3·min). The light beam was unfiltered and not collimated. After irradiation the polymer was washed with benzene and methanol as previously described [4]. Homopolymer was determined by a modification of the Kline procedure [17].

Gamma Irradiation

Irradiations were performed in stoppered glass tubes with monomer and solvent added to a total volume of 8 mL and cellulose acetate strips or gel beads completely immersed. Irradiations were performed in the spent Fuel Element Facility at the Australian Atomic

TABLE 1. Gamma Ray Grafting of Styrene to Polypropylene and Polyethylene Films in Methanol[a]

Styrene (% v/v)	Graft (%)[b]	
	Polypropylene	Polyethylene
20	57 (1.2)	13 (0.6)
30	86 (1.8)	- -
40	64 (2.0)	80 (1.6)
60	- -	65 (1.4)
70	33 (2.7)	- -
100	19 (1.2)	- -

[a] Total radiation dose was 2.0×10^5 rd at 1.84×10^5 rd/h.
[b] Data in parenthesis, homopolymer yield (%).

Energy Commission to a total dose of 2.0×10^5 rd at a rate of 1.84×10^5 rd/h. Afterwards, the cellulose acetate was extracted with xylene for 24 h and graft and homopolymer determined by the modified Kline procedure [17].

RESULTS

Polyolefins

In gamma radiation copolymerization of styrene to polypropylene (Table 1) a gel peak is exhibited at 30% styrene concentration for the radiation dose and dose rate used, and the degree of copolymerization declines gradually from this monomer concentration to neat monomer. Copolymerization to polypropylene is only slightly higher than to polyethylene although it is apparent in both systems that grafting in low monomer concentration solutions is preferred since the degree of homopolymerization (shown in parenthesis) is low in both systems. Also, yields are highest in these low monomer concentrations.

There are similarities between this gamma radiation grafting process and the photosensitized process (Table 2) where a gel peak is exhibited at 30% styrene concentration. Photosensitized grafting of styrene in methanol to polypropylene, however, is very specific to the nature of the sensitizer. Benzoin ethyl ether (BEE) and biacetyl (BAC) are the most effective of the sensitizers studied (Table 2), but in the absence of sensitizer, copolymerization only occurs in neat monomer with the UV conditions used.

TABLE 2. UV Grafting of Styrene to Polypropylene Films in Methanol[a]

Styrene (% v/v)	Graft (%) with sensitizer (1%)[b]		
	O	BEE	BAC
20	0	49	13
30	0	150	108
40	0	34	49
60	0	32	38
80	0	26	21
100	16	25	-

[a] Irradiations at 30 cm from 90 W high pressure UV lamp, exposure time = 16 h.

[b] BEE = benzoin ethyl ether; BAC = biacetyl. Sensitizer concentration, 1% w/v. Uranyl nitrate and benzophenone gave essentially no graft.

TABLE 3. UV Grafting of Styrene to Polypropylene Films in Miscellaneous Solvents[a]

Styrene (% v/v)	Graft (%)[b]				
	MeOH	n-BuOH	n-HpOH	DMF	DMSO
20	49 (20.1)	62	82	0	0
30	150 (24.5)	263	149	-	-
40	34 (14.7)	119	65	6	10
60	32 (-)	36	46	12	71
80	26 (-)	27	27	21	36

[a] Irradiations at 30 cm from 90 W high pressure UV lamp, exposure time = 16 h; benzoin ethyl ether sensitizer (1% w/v).

[b] MeOH = methanol; n-BuOH = n-butanol; n-HpOH = n-heptanol; DMF = dimethylformamide; DMSO = dimethylsulfoxide; data in parentheses, homopolymer yield (%).

TABLE 4. UV Grafting of Styrene to Polyethylene Films in Miscellaneous Solvents[a]

Styrene (% v/v)	Graft (%)[b]			
	MeOH	n-HpOH	DMF	DMSO
20	42 (-)	53	0	11
30	137 (-)	140	-	-
40	63 (-)	107	6	52
60	32 (15.6)	31	22	33
80	41 (21.3)	23	25	29

[a] Irradiations at 30 cm from 90 W high pressure UV lamp, exposure time = 16 h; benzoin ethyl ether sensitizer (1% w/v).

[b] MeOH = methanol; n-HpOH = n-heptanol; DMF = dimethylformamide; DMSO = dimethylsulfoxide; data in parentheses, homopolymer yield (%).

For other solvents (Table 3), grafting with BEE in n-butanol is significantly higher than in methanol while in n-heptanol grafting is only marginally higher than in methanol. Yields are lower in dimethylformamide grafting. Even in the absence of a value for 30% styrene concentration, there appears to be no gel peak but instead, a steady increase in yield to 80% styrene concentration. Homopolymerization (shown in parentheses) competes with the grafting of styrene to polypropylene in methanol solution to a higher degree than that observed in gamma radiation grafting (Table 1).

In dimethylsulfoxide a gel peak is evident at 60% styrene concentration. Similar trends are observed for styrene grafted to polyethylene (Table 4) in these solvents although in dimethylsulfoxide the gel peak appears to be exhibited at 40% rather than 60% styrene concentration.

Of further significance is the high reactivity of 4-vinylpyridine, especially when dissolved in pyridine (Table 5). This monomer exhibits a gel peak at 60% concentration in pyridine and at 80% in methanol. Relative to styrene and methyl methacrylate, 4-vinylpyridine grafts to polypropylene more efficiently with UV than with ionizing radiation, a result of significant practical value. Methyl methacrylate is also UV grafted to polypropylene (Table 5) although homopolymerization is dominant. This generally leads to difficulty in recovering copolymer in uncontaminated form especially at high grafting yields. At monomer concentrations of 20 and 30%, low grafting is achieved but the copolymer can be quantitatively recovered.

TABLE 5. UV Grafting of Methyl Methacrylate (MMA) and 4-Vinylpyridine (VP) to Polypropylene Films[a]

	Graft (%) with sensitizer (1%)			
	MMA		VP	
Monomer (% v/v)	BEE[b]	UO_2^{2+} [c]	BEE[b,g]	BEE[d,g]
20	8[e]	2	12	35
40	63[f]	2	43	107
50	-	-	-	348
60	89[f]	14	87	504
70	-	-	118	419
80	-	8	164	343
90	-	-	78	-
100	-	-	56	73

[a] Irradiations at 30 cm from 90 W high pressure UV lamp.
[b] Benzoin ethyl ether in methanol.
[c] Uranyl nitrate in methanol.
[d] Benzoin ethyl ether in pyridine.
[e] Irradiation time = 3.5 h.
[f] Irradiation time = 6 h.
[g] Irradiation time = 16 h.

TABLE 6. Radiation Grafting of Styrene to Cellulose Acetate Films in Alcohols[a]

	Graft (%)[b]			
Styrene (% v/v)	MeOH	EtOH	n-PrOH	n-BuOH
20	21	17 (1.7)	16	6
30	25	30 (2.0)	26	9
40	25	42 (2.1)	35	13
60	19	43 (2.0)	41	23
80	28	44 (2.3)	41	10

[a] Total dose of 2.0×10^5 rd at 1.84×10^5 rd/h.
[b] MeOH = methanol; EtOH = ethanol; n-PrOH = n-propanol; n-BuOH = n-butanol; data in parentheses, homopolymer yield (%).

TABLE 7. Radiation Grafting of Styrene to Cellulose Acetate Films in Miscellaneous Solvents[a]

Styrene (% v/v)	Graft (%)[b]				
	ACET	DMF	CH_2Cl_2	$CHCl_3$	CCl_4
20	0	8	3	0	0
30	3	-	6	6	0
40	2	14	7	10	0
60	21	20	20	26	0
80	38	0	27	4	0

[a] Total dose of 2.0×10^5 rd at 1.84×10^5 rd/h.

[b] ACET = acetone; DMF = dimethylformamide; CH_2Cl_2 = methylene chloride; $CHCl_3$ = chloroform; CCl_4 = carbon tetrachloride.

Cellulose Acetate

Styrene is readily grafted to cellulose acetate films in a range of alcohol solutions (Table 6) at a total dose of 0.2 Mrd. Copolymerization is marginally highest in ethanol and gradually decreases to n-butanol. Gel formation is only observed in n-butanol (at 60% styrene concentration), results with the other three alcohols being consistent with those observed previously in unacetylated cellulose [18].

Homopolymerization (shown in parentheses) is low and also consistent with that observed previously in solutions with cellulose [18].

In dimethylformamide a gel peak is observed (Table 7) at 60% styrene concentration but, in contrast to the observation of Stannett et al. [19] for a 1 Mrd dose, no grafting occurs for 80% styrene concentration at this dose of 0.2 Mrd. No gel peak occurs in acetone although one is observed in chloroform at 60% styrene concentration (Table 7). Furthermore, in chlorinated methanes the degree of copolymerization reactivity decreases from methylene chloride and chloroform to carbon tetrachloride.

In combination solvent systems incorporating acetone or chloroform with methanol or ethanol (Table 8), styrene grafting to the cellulose acetate films is dependent on the solution composition. Grafting in acetone-methanol is very similar to that in acetone-ethanol with optimum grafting yield observed in solutions containing 60% acetone-alcohol concentration. Furthermore, gel peaks are observed in 60% acetone-alcohol solutions at 60% styrene concentration but not in alcohol solutions incorporating 40% acetone or 60% chloroform.

TABLE 8. Radiation Grafting of Styrene to Cellulose Acetate Films in Mixed Solvents[a]

Styrene (% v/v)	Graft (%)[b]		
	40A	60A	60C
		Methanol	
40	0	14	0
60	8	49	12
80	21	23	24
		Ethanol	
40	0	19	0
60	10	47	12
80	32	20	26

[a] Total dose of 2.0×10^5 rd at 1.84×10^5 rd/h.

[b] 40A = 40% acetone-alcohol, 60A = 60% acetone-alcohol, 60C = 60% chloroform-alcohol.

TABLE 9. Radiation Grafting of Styrene to Cellulose Acetate Gel Beads in Mixed Solvents[a]

Styrene (% v/v)	Graft (%)[b]		
	40A	60A	60C
		Methanol	
40	0	0	0
60	0	13	0
80	0	11	0
		Ethanol	
40	0	0	0
60	0	0	0
80	6	20	3

[a] Total dose of 2.0×10^5 rd at 1.84 rd/h.

[b] 40A = 40% acetone-alcohol, 60A = 60% acetone-alcohol, 60C = 60% chloroform-alcohol.

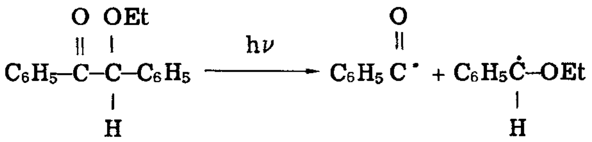
With the exception of one acetone-ethanol solution, styrene grafting to cellulose acetate gel beads (Table 9) is much less successful than to films. This is consistent with an observed absence of styrene grafting to gel beads in single solvent-monomer systems [20].

DISCUSSION

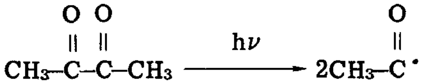
Grafting to Polyolefins

The ability to photograft monomers such as styrene to trunk polymers by the simultaneous method is important for the purpose of insolubilization of reagents since the technique provides less energetic complementary copolymerization than ionizing radiation initiation.

Neither uranyl nitrate nor benzophenone are very successful as sensitizers under the simultaneous UV irradiation conditions used, these data being consistent with the results of earlier workers [14-16]. In this respect it is important to note that, of the organic sensitizers, both benzoin ethyl ether and biacetyl absorb UV to give radicals directly capable (Eqs. 1 and 2) of initiating polymerization.



$$C_6H_5{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{\overset{\overset{OEt}{|}}{C}}{-}C_6H_5 \xrightarrow{h\nu} C_6H_5\overset{\overset{O}{\|}}{C}{}^{\bullet} + C_6H_5\underset{\underset{H}{|}}{\dot{C}}{-}OEt \qquad (1)$$



$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow{h\nu} 2CH_3{-}\overset{\overset{O}{\|}}{C}{}^{\bullet} \qquad (2)$$

whereas benzophenone forms excited state species upon UV irradiation. With benzoin ethyl ether and biacetyl the grafting reaction thus appears to be free radical initiated. This is to be expected since in many aspects the data are remarkably similar to copolymerization by ionizing radiation, a process known to be predominantly free radical in nature at room temperature and above [21]. The mechanism of the UV grafting appears to involve swelling of the film by the monomer when a nonswelling solvent such as a low molecular weight alcohol is used, with subsequent diffusion of radicals from the sensitizer into the film where hydrogen abstraction reactions lead to grafting sites. Excited states of monomer can also directly participate in site formation in a manner similar to that already proposed for analogous UV grafting in wool [10] and cellulose [9].

The high grafting yields obtained with styrene and 4-vinylpyridine are further evidence to support the concept that the ability of a monomer to swell the polyolefin is an advantage. Swelling also helps the radical species from the sensitizer to diffuse into the trunk polymer to create grafting sites. Some sensitizer will also be incorporated into the film in this manner, however, especially if low concentrations of sensitizer are used initially, the level appears to be orders of magnitude lower than with the technique of preincorporation previously reported [16]. Swelling of the trunk polymer is also important in the gamma-ray initiated grafting of styrene, 4-vinylpyridine, and methyl methacrylate to the polyolefins. However, one unique problem not applicable to ionizing radiation is that of competing homopolymerization. In the simultaneous UV grafting method, as homopolymerization occurs, the reaction solution may become turbid, thus terminating copolymerization at an early stage.

In terms of the usefulness of copolymerization for reagent insolubilization, the present UV data are of fundamental interest since certain monomers such as 4-vinylpyridine graft in higher yield than with ionizing radiation. Furthermore the data are of practical significance since this photosensitized method is particularly amenable to the large-scale preparation of copolymers.

Grafting to Cellulose Acetate

The grafting characteristics of styrene to cellulose acetate are similar to those for cellulose reported earlier [18]. The data suggest that radiolytically produced hydrogen atoms may influence the reaction pathway. Thus, for chlorinated hydrocarbon solvents the presence of protons in these solvent molecules is necessary to achieve grafting under the conditions of gamma irradiation used.

A significant factor in these studies is the poor grafting yields obtained in the styrene-gel bead systems. With some important exceptions, enhancement of swelling of the gel beads using combination solvents results in little improvement in grafting yield. The presence of moisture was at first considered to be a likely cause of this effect since the beads, normally stored in cold water, needed to be washed repeatedly with dry ethanol prior to grafting. However, the absence of grafting seems to be associated with another, still to be determined, effect as significant grafting to cellulose acetate films occurs in ethanol solutions containing up to 4% added water.

The problem of lower grafting yields of styrene to gel beads is under further investigation. These beads possess large surface area, porosity, good mechanical strength and resilience, and have been used successfully for treatment of nonhomogeneous citrus juices in a continuous fluidized bed column process [22] without mechanical breakdown or clogging. Cellulose acetate gel beads, therefore, may have considerable potential as a support for the insolubilization of catalytic reagents.

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