An Investigation of the Nitroxide-Mediated Preirradiation Grafting of Styrene onto PFA

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ABSTRACT: Simultaneous and preirradiation grafting of styrene onto fluorinated polyolefins does not enable control of the molecular weights or polydispersities of the styrene grafts. The nitroxide-mediated grafting of styrene onto PFA with TEMPO and TEISO using a preirradiation method has been investigated as a means of controlling the graft properties and especially to produce grafts with improved suitability for SPOC. The yields of graft were found to be in the range 15−20% for nitroxide concentrations between 5×10^{-3} and 2×10^{-2} M and were similar for the two nitroxides studied. Raman mapping was used to obtain the depth profile for the styrene grafts. The grafts were found to be principally located within the PFA substrate, and little graft was formed at the PFA surface. Fmoc loading tests were performed to assess the suitability of the grafted PFA as a support for SPOC, but these showed no significant loading was achieved, thus indicating that the graft properties are not suitable for SPOC. However, the study has important implications for the applications of PFA-grafted polymers in other areas, such as chemically resistant ion-exchange and separation membranes.

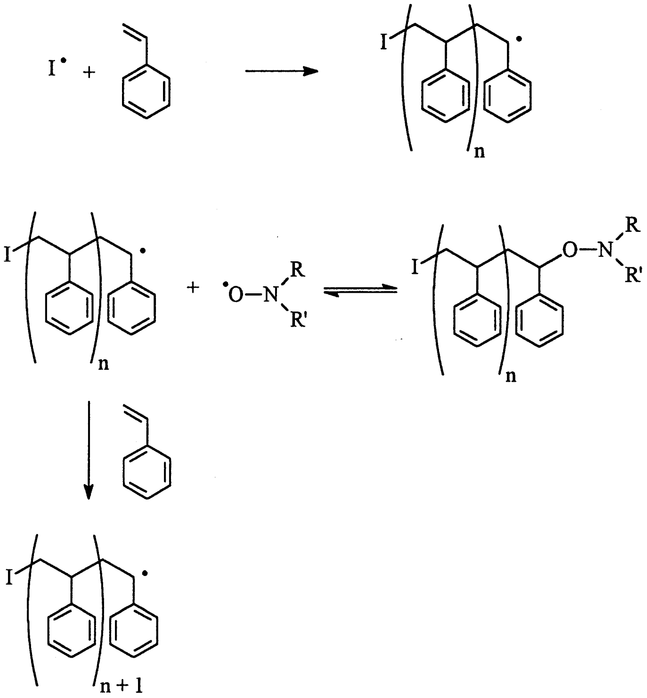
Introduction

Controlled or “living” polymerizations have aroused intense interest from polymer chemists in the past few years due to the prospect of alleviating many of the limitations of conventional free radical polymerization. Some of these limitations arise from the lack of control of the process, leading to structures with undefined molecular weight distribution, structure, and end groups. Controlled polymerizations offer the prospect of narrow-polydispersity homopolymers, high-purity block copolymers, and end-functionalized polymers.[1]

The forms of controlled polymerizations available include nitroxide-mediated “living” free radical polymerization,[2] atom transfer radical polymerization (ATRP),[3−5] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[6,7] The synthesis of well-defined polymers by “living” free radical polymerization (LFRP) techniques was first demonstrated by Rizzardo and co-workers in the early 1980s for styrene using stable nitroxide free radicals.[2] Nitroxide species, when used in certain polymerizations, act to mediate the reactivity of the growing polymer chains by forming thermally unstable alkoxy amine chain ends. An equilibrium is formed between the dormant alkoxy amine chain ends and active free radical chain ends upon homolysis of the carbon−oxygen bond of the alkoxy amine (see Scheme 1). In the free radical state, monomer units can add before the growing chains are reversibly terminated by the nitroxide radical. The reversible reaction between active and dormant chain ends gives the polymerization a “living” character.

LFRP techniques have enabled control of chain ends, molecular weight, and macromolecular architecture for the polymerization of a number of monomers.[8−11] The polydispersity attainable with nitroxide-mediated polymerization is typically below 1.5, whereas for conventional radical polymerization with termination by chain transfer or disproportionation the theoretical polydispersity is approximately 2.0 or 1.5 for combination termination.[1,12]

Scheme 1. Proposed Mechanism for Nitroxide-Mediated Polymerization



Normally nitroxide-mediated LFRPs are performed by adding an initiator and a nitroxide to a bulk monomer followed by heating at a temperature between 353 and 408 K. At these temperatures the alkoxy amine

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will readily dissociate so that additional monomer units can add to the growing chains before being capped by the nitroxide. This process of dissociation, monomer addition, and reassociation continues until either all the monomer is consumed or the reaction is stopped.

The linear, narrow molecular weight distribution polymers attainable using LFRP potentially have applications for controlled grafting polymerizations of styrene monomer onto matrix polymers for use as ion-conducting membranes or in solid-phase organic chemistry (SPOC). Recently, workers at the Park-Davis laboratories have reported using nitroxide-mediated LFRP to graft linear polymers bearing functional groups onto a cross-linked polystyrene (PS) core (Merrifield resin).[13] These resins, called “Rasta” resins, prepared using styrene and 3-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) monomers to incorporate isocyanate functional groups, exhibited higher loading than Merrifield resin. Fluorescence probes bound to the isocyanate moieties showed that these groups were distributed throughout the entire resin, suggesting that during the LFRP step the reagents were free to diffuse throughout the Merrifield resin.[14] Control of the polymerization allows the customized spacing of the functional groups through judicious choice of the comonomers and fine-tuning of solvent affinity. Other high-loading SPOC resins have also been reported which are based on attaching dendrimers bound to a resin core,[15] but in this case the dendrites were part of the linker groups and not the polymeric substrate.

Graft copolymers have also been prepared using LFRP by including an alkoxy amine in the backbone of the base polymer during the synthesis step.[16] Grafting involves heating the backbone polymer with incorporated alkoxy amine groups in the presence of a monomer to form a graft copolymer with controlled molecular weight. Other “living” techniques have also been used to prepare graft copolymers. Recent examples include the use of ATRP to control grafting of styrene to the fluoropolymer PVDF[17] and the use of RAFT to graft various monomers to polypropylene.[18]

A novel method for using nitroxide-mediated LFRP to graft to a preexisting polymer was recently demonstrated by Miwa et al.[19] Using the preirradiation peroxy grafting method, these workers were able to graft styrene to polypropylene with control of the molecular weight of the graft using the classical nitroxide, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). These workers initially irradiated polypropylene in the presence of air to create hydroperoxy groups. Styrene and TEMPO were then added to the irradiated polypropylene and heated. The proposed mechanism involved decomposition of the hydroperoxy groups to form oxy radicals, which were capable of initiating the graft copolymerization of styrene.

A consequence of using oxy radicals as the initiating species is that an ether group would be formed between the polymer substrate and the graft. Miwa et al. exploited the presence of these acid-sensitive ether groups by selectively cleaving the graft through the ether bond by treatment with trifluoroacetic acid in toluene. This allowed the measurement of the MWD of the cleaved graft by SEC analysis. The MWD of the graft and of the free homopolymer also formed during the reaction were similar. The end groups of the cleaved PS were identified as hydroxy groups by NMR, thereby proving that the PS isolated was not a product of thermal autoinitiation. (The hydroperoxy groups on the polypropylene decomposed to form $^{\bullet}$OH radicals that are capable of initiating homopolymerization of styrene.[20] Thus, while some of the homopolymer will be formed from reaction of styrene with these $^{\bullet}$OH radicals, much of the homopolymer may also result from thermal autoinitiation reactions.[21])

The preirradiation peroxy method has drawbacks when grafting to polymers such as PFA, where the application is say for conducting membranes or SPOC supports. First, PFA becomes very brittle when irradiated in air.[22] Second, the presence of acid-sensitive ether groups is undesirable when the graft copolymer is used for SPOC, as strong acid treatment is regularly used to deprotect groups during synthetic steps.

Recently, there has been significant interest in the use of styrene-grafted extrudable fluoropolymers, such as PFA, for the manufacture of high-temperature matrix supports for SPOC.[23] However, previously only the conventional simultaneous or preirradiation grafting of styrene onto PFA has been reported. In the current work the grafting of styrene in the presence of nitroxides, as a means of modifying the nature of the grafting processes, has been investigated using a preirradiation method under vacuum. The suitability of the grafted PFA for SPOC was tested by measuring the loading achieved when a standard linker system was used to functionalize the polystyrene graft.[24,25]

Experimental Section

Styrene (Fluka) was passed through a column of alumina oxide and then distilled under reduced pressure just prior to use. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) (Aldrich) was used as received. 1,1,3,3-Tetraethylisoindolin-2-yloxyl (TESIO) was kindly donated by Urs Wermuth from Griffith University and recrystallized from *n*-pentane before use. Dichloromethane used for washing was reagent grade and used as received.

Grafting. PFA (Du Pont, code TE 7132), injection-molded lanterns (see Figure 1) for SPOC, with rings of 0.5 mm in thickness, were supplied by Mimotopes. Grafting of styrene to the PFA lanterns was performed using the preirradiation method under vacuum. The lanterns were first placed in Pyrex tubes and evacuated at 1×10^{-2} Pa for 24 h, then the tubes were sealed, and the samples were irradiated at 300 K in a 220 Nordian Gammacell to a dose of 20 kGy at a dose rate of 4.7 kGy h^{-1}. Nitroxide solutions were prepared by dissolving either TEMPO or TEISO in styrene (5 mL) to the desired concentration. The nitroxide solutions were added to the irradiated PFA under a stream of nitrogen gas at room temperature through a tap fitted with rubber O-rings. The solutions were then degassed by three freeze−pump−thaw cycles and sealed under vacuum by melting a narrow neck in the glass. The grafting of the styrene to the irradiated PFA was investigated first at room temperature and then at 373 ± 2 K by heating the tubes in an oil bath. After reaction, the PFA lanterns were thoroughly washed for 24 h with hot dichloromethane in a Soxhlet extractor to remove any remaining styrene and occluded homopolymer. (After grafting the lanterns could be swollen by dichloromethane.) The grafted PFA samples were then dried under vacuum and weighed to measure the graft yield. The graft yield was expressed as a percentage of the initial weight of the PFA lantern.

Differential Scanning Calorimetry. A Perkin-Elmer DSC7 was used to perform DSC on sections of the grafting rings cut using a blade. Samples were heated under a nitrogen atmosphere from 323 to 633 K at 40 K min^{-1}. For the ungrafted samples, the heat of fusion was taken from the peak area under the melting endotherm. For grafted samples, where the amorphous PS component dilutes the crystallinity, the heat

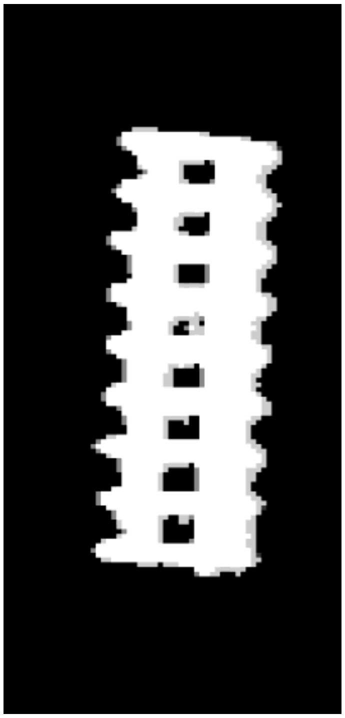

Figure 1. Photograph of a Mimotopes lantern. Characteristics of the cylindrical lantern: diameter 5 mm, length 13 mm, mass ≈ 0.16 g.

of fusion for just the PFA component was calculated as

$$\Delta H_{\mathrm{PFA}} = \frac{\Delta H_{\mathrm{total}}}{W_{\mathrm{PFA}}/W_{\mathrm{PFA+PS}}}$$

where W_{PFA} and $W_{\mathrm{PFA+PS}}$ are the weight of the samples before and after grafting, respectively.

Microprobe Raman Spectroscopy. Microprobe Raman spectroscopy was performed using a Renishaw System 1000 Raman spectrometer (Renishaw plc. Wotton-under-Edge, UK) equipped with Renishaw laser diode emitting at 785 nm. An Olympus MD Plan microscope with a 50× objective lens was used to focus the laser to a spot size of approximately 1 μm. Each spectrum was collected in the static mode for 20 s in the range 700−1200 cm^{-1}. Graft copolymer samples to be analyzed were mounted on a microscope slide and held in place with generic putty. The Raman maps were produced by acquiring a series of spectra across the sample using an automated movable stage.

SPOC Loading Tests. The performance of styrene-grafted PFA for use of a matrix for SPOC was assessed using the standard Fmoc-Rink loading test procedure described by Maeji et al.[21] The details of the test procedure have been described by us previously[25] for assessing the performance of styrene-grafted PFA samples. This loading test provides a measure of the efficiency with which the grafted polystyrene can be coupled via a linker with another molecule for use in organic synthesis. The loading for a grafted PFA sample is expressed in terms of micromoles of Fmoc groups coupled to the grafted styrene chains.

Results and Discussion

Nitroxide Effect on Graft Yield. The rate-determining step in conventional nitroxide LFRPs is the bond dissociation of the alkoxy amine group.[26,27] The rate of homolysis of the NO−C bond of the alkoxy amines is known to depend on a combination of steric compression around the NO−C bond, the stabilities of the radicals formed, and polar factors.[1] By varying the R and R′ groups of the nitroxide shown in Scheme 1, the reactivity of the nitroxide can be modified.[10,11,21,28] Of the two nitroxides used for this work, the rate of homolysis of the NO−C bond is known to be more rapid for TEISO than for TEMPO (the structures are shown in Figure 2).[28] In the case of the postirradiation grafting of styrene onto PFA in the presence of a nitroxide, the original initiating radical I$^{\bullet}$ in Scheme 1 would be a polymer chain radical.

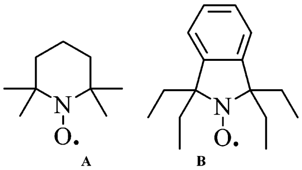

Figure 2. Structures of TEMPO (A) and TEISO (B).

The concentration of the nitroxide used in a thermally initiated styrene polymerization influences the conversion and molecular weight distribution of the PS formed[9,29] as well as the polymerization rate. At very low nitroxide concentrations the system behaves like a traditional free radical polymerization, giving rise to high-conversion polymers with a high molecular weight and wide polydispersity. If excess nitroxide is used, there is a definite incubation period, but once all of the nitroxide is consumed, polymers with a low molecular weight and a narrow polydispersity are formed, but at a lower rate than a conventional thermally initiated polymerization.

Like all fluoropolymers based upon tetrafluoroethylene, PFA is an inert polymer that does not swell in common solvents, including styrene monomer. However, it is possible to graft styrene to PFA by in situ radiation grafting,[23] in which case the grafted chains can penetrate through relatively thick samples. This occurs because the grafting reaction proceeds via a grafting front process in which grafted chains allow styrene to swell the modified matrix, so that the depth of the graft increases with the grafting time.

PFA can also be grafted with styrene using a preirradiation procedure, but the grafting rate is much lower due to the relatively small active radical concentration in the preirradiated polymer. However, because of the inertness of PFA to solvents, it is not possible to carry out a preirradiation grafting polymerization by first trapping the radicals by diffusing a nitroxide into the matrix in solution at room temperature and then subsequently adding the styrene monomer. Therefore, in the current study the nitroxides have been dissolved in the styrene in an attempt to initiate a nitroxide-mediated polymerization. Thus, the procedure adopted in this work was similar to that used by Miwa et al.[19] for grafting styrene onto polypropylene, but the radicals initiating the grafting reaction are carbon and not oxygen centered radicals.

The effect of the nitroxide concentration on the grafting of styrene to preirradiated PFA was investigated by using a range of nitroxide concentrations in styrene, from neat styrene to styrene containing up 3.6 × 10^{-2} M nitroxide. At the lowest concentration of nitroxides used (4.6 × 10^{-3} M) the excess of nitroxide over the polymer radicals present in the lanterns was greater than 100-fold.

When the reaction was performed at room temperature with 4.6 × 10^{-3} M TEMPO, no grafting or homopolymerization was observed, even after 100 h, but the same reaction at room temperature in the absence of

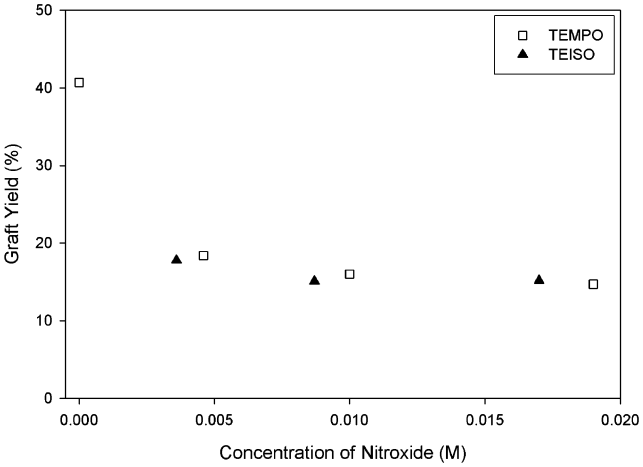

Figure 3. Graft yield for different nitroxide concentration when grafting styrene to PFA at 373 K: (■) TEMPO; (▲) TEISO. The grafting time was 40 h.

any nitroxide led to a graft yield of 65 % after 40 h. Thus, when a nitroxide is present along with the styrene in the grafting medium at room temperature, the nitroxide inhibits polymerization by forming a stable alkoxy amine either by reaction with PFA chain radicals or with styrene propagating radicals formed by addition of styrene to the PFA radicals. Unfortunately, it was not possible to identify whether just one or both of these reactions occur. However, the absence of any graft at room temperature is undoubtedly due to the trapping of radicals by the nitroxide, and the high stability of the resulting alkoxy amines at room temperature inhibits polymerization.

Although no graft was formed at room temperature, by increasing the temperature of the reaction mixture to 373 K, where the stability of the alkoxy amines is much lower, a grafting polymerization begins. Previous studies of styrene polymerizations have demonstrated that at 373 K the alkoxy amines dissociate to release the styrene propagating radicals,[1,2] as described in Scheme 1. Thus, at 373 K the reaction mixture becomes “living”, as demonstrated by the results in Figure 3, and the polymerization rate is much lower than that observed in the absence of the nitroxide, as would be expected for a nitroxide-mediated polymerization. The yield of the graft was found to increase with grafting time at 373 K, but the yield plateaued at a grafting time of 40 h for a preirradiation dose of 20 kGy.

The concentration of the nitroxide was found to affect the grafting rate, and for increasing concentrations of TEMPO and TEISO the graft yield at 373 K decreased, as shown in Figure 3. Incorporation of either TEMPO or TEISO at a concentration of 3.6×10^{-3} M causes a significant decrease in the graft yield from approximately 40% for pure styrene to less than 20% after 40 h in the presence of the nitroxide. However, above 1×10^{-2} M nitroxide a further increase in the concentration had little effect on the overall graft yield. The fact that the graft yield at 40 h does not decrease as the nitroxide concentration increases approximately 4-fold from 1×10^{-2} to 3.6×10^{-2} M indicates that the role of the nitroxide is not to inhibit polymerization by reacting with PFA radicals to form a dead alkoxy amine on the PFA chain.

Grafted PFA swollen with styrene represents a very viscous medium for grafting, which may explain why the degree of grafting with TEISO was not higher than that for TEMPO, as may be expected from the more labile NO−C bond in the alkoxy amine formed by TEISO. However, it is possible that the nitroxide mediation of the graft polymerization of styrene is diffusion-controlled in these viscous media. Thus, it is independent of the NO−C bond stability. Lutz et al.[30] have reported experimental validation of kinetic models proposed by Fischer[31,32] for nitroxide-mediated polymerizations. They found that at high conversion the experimental kinetics deviated from theoretical predictions, and they suggested that the behavior was due to viscosity effects.[30] For grafting of styrene to PFA, the highly viscous grafting regions would mimic a polymerization at high conversion, so it is not surprising that the graft yield for TEMPO and TEISO do not obey predictions based on the NO−C bond strengths alone.

Characterization of the Grafts. The distribution of the graft and the accessibility of the graft to reagents are important factors for ion-exchange membranes and for grafted supports used for SPOC. To measure the distribution of the graft, microprobe Raman spectroscopy has been used to map cross sections of the grafted supports.[25] The well-resolved Raman shifts at 999 cm^{-1} for PS and 734 cm^{-1} for PFA were used to assess the PS distribution in the graft copolymer.[25] The Raman map of a cross section of PFA-*g*-PS with 4.6×10^{-3} M TEMPO is shown in Figure 4. The map for PFA grafted under the same conditions, only without any nitroxide, is shown in Figure 5. Without nitroxide added, the peak due to the PS graft was more intense relative to the peak due to PFA, while the opposite was true when nitroxide was used. Since the radical concentration and distribution in the preirradiated PFA are fixed by the radiation dose, a lower relative intensity of the PS peak in the presence of nitroxide is consistent with a lower molecular weight of the grafted chains, as would be expected for a nitroxide-mediated polymerization.

TEMPO has a peak in the Raman spectrum at 847 cm^{-1} (see Figure 6) which was not observed in the map spectra. This suggests that either the alkoxy amine end groups were not present in a high enough concentration to observe in the grafted PFA or the alkoxy amine chain ends were lost as a result of chain termination reactions. On the basis of our previous ESR study of irradiated PFA,[33] if every radical present in the preirradiated PFA led to the formation of a styrene graft, the graft concentration would be very low, being less than 10^{-6} mol g^{-1} or less than one grafted chain for every 10^{4} CF bonds in the polymer. So, not to find any evidence for a peak at 847 cm^{-1} in the Raman spectra is not surprising. The solid-state ^{19}F and ^{1}H NMR spectra of the grafted polymers were also examined for evidence of graft points, but none was found. However, here again the low concentration of the grafted chains and the shorter relaxation time of the fluorine and proton atoms attached at the graft points are the reasons for not being able to identify them.

Thus, the identification of the grafted styrene chain ends could not be used to obtain a measure of the average molecular weight of the styrene chains grafted onto the PFA. Therefore, it has not been possible to obtain direct molecular weight evidence for the control of the grafting reaction through a nitroxide-mediated polymerization. However, Miwa et al.[19] have shown for the grafting of styrene onto polypropylene in the presence of a nitroxide that indeed the nitroxide does allow control of the molecular weight and molecular weight

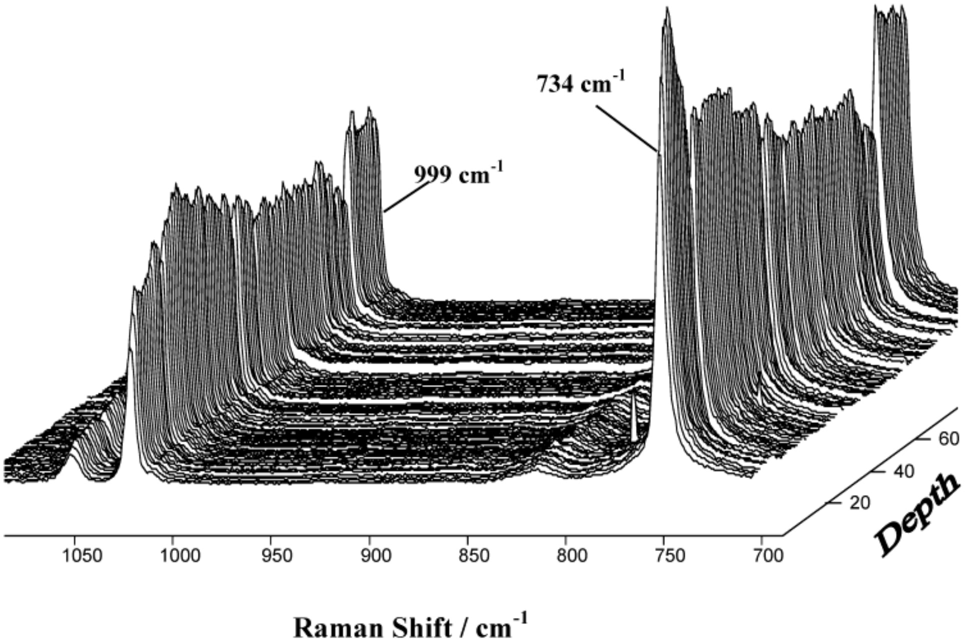

Figure 4. Raman spectra vs depth of a section through a PFA lantern grafted with styrene containing 4.6 × 10^{-3} M TEMPO. The depth increment between spectra is 2 μm.

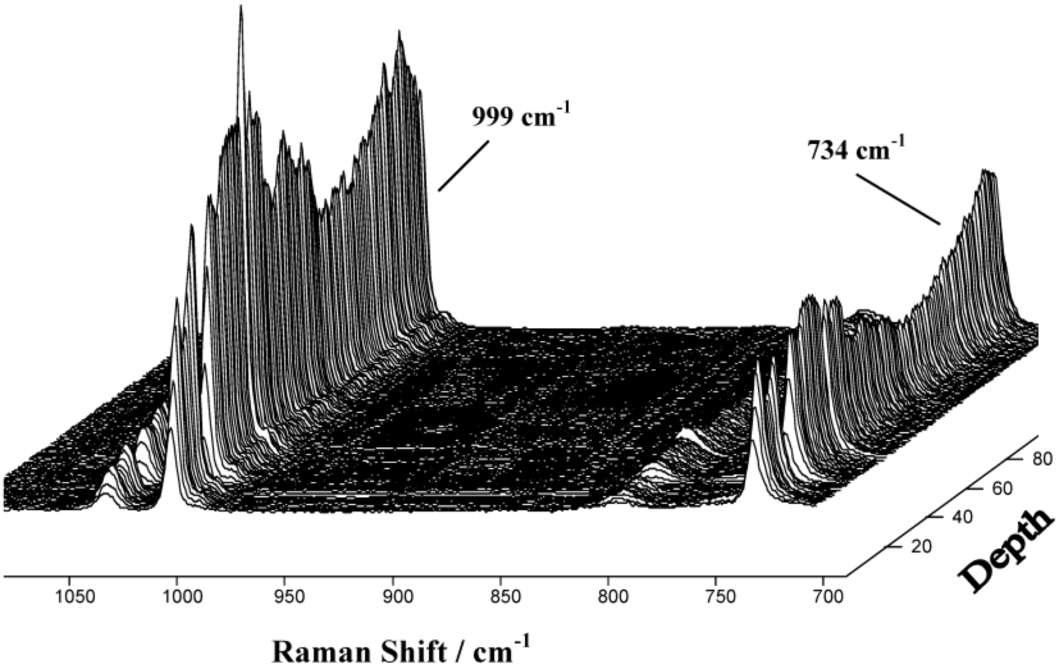

Figure 5. Raman spectra vs depth through a cross section of a PFA lantern grafted using neat styrene monomer. The depth increment between spectra is 2 μm.

distribution of the grafted styrene chains. Therefore, it seems reasonable to infer that the grafting took place via a similar mechanism in the present case.

A semiquantitative measure of the distribution of PS graft in PFA was calculated from the Raman maps using the method reported previously[25] and is shown in Figure 7. The penetration profiles have been expressed as the distance into the cross sections as a percentage of the total thickness, since each grafted sample had a slightly different thickness. It was assumed that the distribution cross sections for the grafted chains were symmetrical across the PFA samples. Figure 7 shows that the mole fraction of PS in the PFA, after grafting for 40 h, decreases with increasing concentration of nitroxide, as would be expected if the polymerizations were living. At 373 K with no nitroxide, the mole fraction of PS was between 0.5 and 0.65, whereas with TEMPO added the fraction of PS dropped to <0.2 mole fraction PS. So the TEMPO has an influence on the grafting reactions within the PFA substrates, presumably lowering the molecular weight of the graft, and increasing the concentration of TEMPO from 4.6 × 10^{-3} to 1.9 × 10^{-2} M results in a decrease in the mole fraction of PS in the grafted PFA.

Grafting performed at 373 K, either with or without nitroxide, led to the graft penetrating the entire substrate. Grafting performed at room temperature, 303 K, in neat styrene without nitroxide resulted in PS only partially penetrating the substrate for the grafting times investigated. At room temperature the grafting reaction

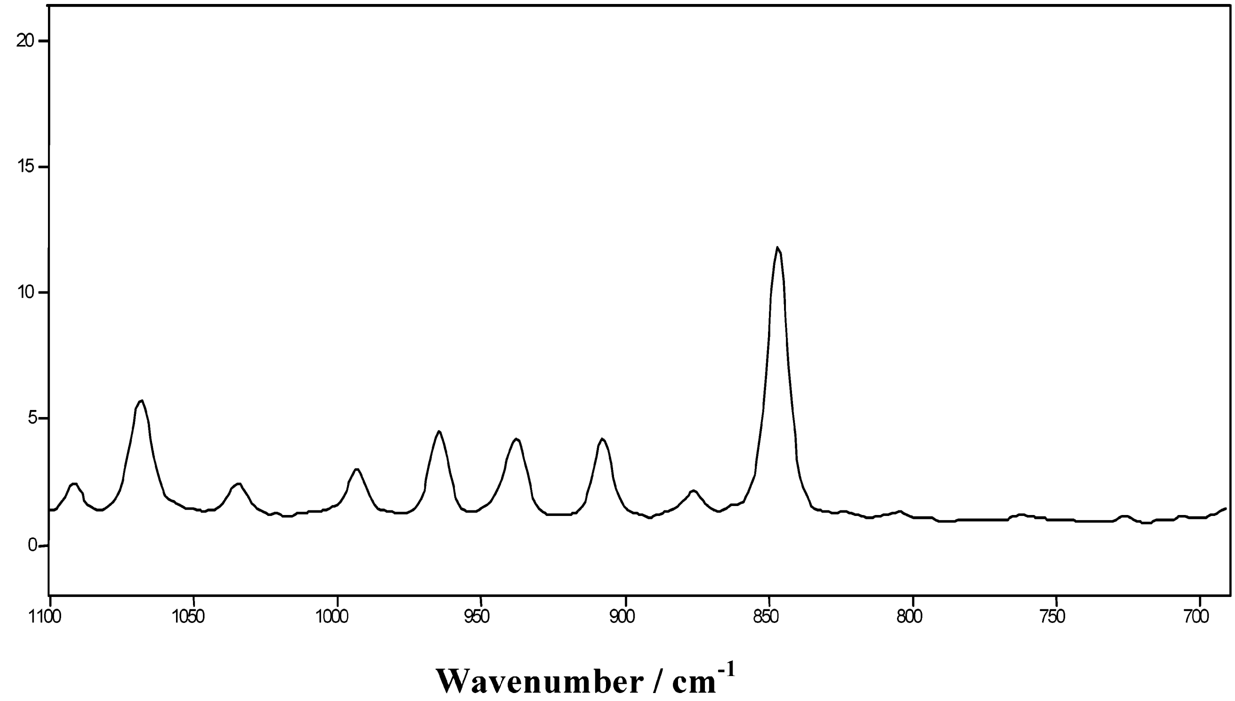

Figure 6. Raman spectrum of TEMPO in the range 700−1100 cm^{-1}.

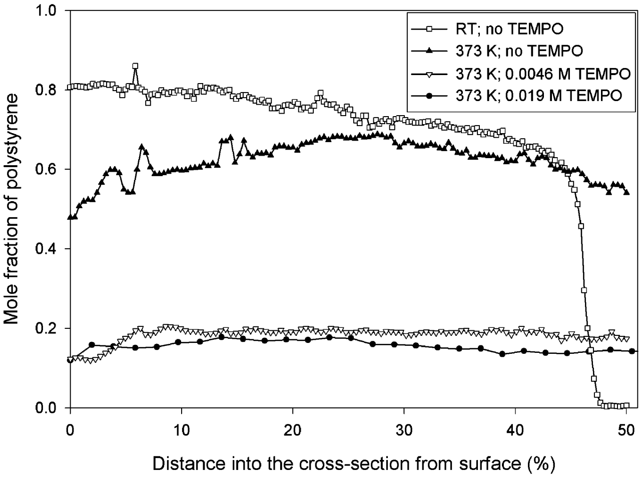

Figure 7. Map of PS graft into PFA substrate. 0% indicates the surface of the graft copolymer, while 50% indicates the midpoint into the cross section.

is controlled by a grafting front mechanism, where grafting begins at the surface and progressively moves into the substrate as the grafted layers swell in the styrene. This was confirmed using Raman microprobe mapping. However, at 373 K the styrene can diffuse through the grafted polymer more readily, so grafting may be occurring throughout the entire substrate for much of the grafting time, thus leading to a more uniform distribution of the concentration of grafted chain through the PFA lanterns.

Role of Radical Stability and Substrate Crystallinity. At 373 K the majority of the radicals created during the irradiation at ambient temperature decompose.[33] For example, at 373 K essentially all of the end-chain ($\sim$C$^{\bullet}$F$_2$) radicals formed in the PFA when it is irradiated under vacuum at room temperature will be lost, and just a portion of the midchain ($\sim$CF$_2$−C$^{\bullet}$F−CF$_2$$\sim$) radicals remain.[33] These midchain radicals are believed to reside either in the crystallites or at the interface regions at the surface of the crystallites. So the grafted styrene chains will reside in the amorphous regions near the crystalline interfaces.

Table 1. Heat of Fusion Determined by DSC (First Run) for PFA Grafted Using Various Conditions

sample	overall heat of fusion ΔH (J g^{-1})	corrected heat of fusion ΔH (J g^{-1})
untreated	26 ± 3	26 ± 3
irradiated only	28 ± 3	28 ± 3
grafted at RT	17 ± 2	28 ± 3
1.9×10^{-2} M TEMPO	24 ± 3	27 ± 3
1.0×10^{-2} M TEMPO	24 ± 3	27 ± 3
4.6×10^{-3} M TEMPO	24 ± 3	28 ± 3
neat sty (no TEMPO)	19 ± 2	26 ± 3

To determine whether the grafting process disturbs the crystallinity of the PFA, the heat of fusion of the crystalline melting endotherm of was measured using differential scanning calorimetry (DSC) both before and after grafting. Since little difference was observed between the graft yield when using TEMPO compared with TEISO, this was done only for the samples grafted in the presence of TEMPO. The heats of fusion calculated from the first DSC scan for untreated, radiation-treated, and grafted lanterns are shown in Table 1. Because of the dilution factor observed for the grafted amorphous PS, a correction factor was used to determine the heat of fusion of the PFA component. The corrected heat of fusion of the PFA is also shown in Table 1. The corrected data show that there is little change in the crystallinity of the grafted samples compared with the untreated or irradiated-only samples. This suggests that there was little disruption of the crystallites during the grafting process. To determine whether the low radiation dose used in the grafting experiment leads to a significant change in the heat of fusion, a control sample that had been irradiated to the same dose as the samples grafted in a vacuum was used. Little difference was seen between the DSC results for this sample and the untreated and grafted samples. It was thus concluded that for the grafting reactions in the presence of nitroxides the initiating species I$^{\bullet}$ in

Scheme 1 are ~CF_2–$C^{\bullet}F$–CF_2~ radicals located principally in the interface regions at the surfaces of the PFA crystallites.

Potential for Use of PFA Matrices for SPOC. To assess the potential for the use of nitroxide-mediated styrene-grafted PFA lanterns for SPOC, a series of Fmoc loading tests were performed on representative grafted lanterns and control lanterns grafted using the simultaneous radiation method. The styrene graft yields were similar for the two sets of lanterns. While an Fmoc loading of 27 μmol per lantern was obtained for the control lanterns, no significant Fmoc loading was obtained for the LFRP grafted lanterns. Although most of the graft was observed by Raman mapping to be below the surface, it had been expected that the extent of surface grafting would be sufficient to allow a measurable loading. However, from the cross-section maps in Figure 7 it can be seen that the mole fraction of PS near the surface of the samples grafted in the presence of nitroxide is less than 0.2. Thus, because the proportion of PS at the surface of the lanterns is low, the grafted substrate cannot swell effectively in the dichloromethane and dimethylformamide/dichloromethane solvents used in the loading tests, so leading to a negligible Fmoc loading.

Therefore, the PFA lanterns grafted by the preirradiation method in the presence of nitroxides are unsuitable for SPOC.

Conclusions

Grafting of styrene to PFA preirradiated in a vacuum using nitroxide-mediated LFRP has been examined. The effect of the nitroxides, TEMPO and TEISO, is to lower the grafting rate and graft yield compared with samples grafted in the absence of nitroxide. Microprobe Raman mapping showed that most of the graft was below the surface, presumably due to the absence of radicals at the surface of the samples following irradiation at room temperature. After grafting styrene to PFA, the crystallinity of the substrate did not change appreciably. This, together with a consideration of the radical stabilities, suggested that the grafting reaction occurred principally at the interface region at the surfaces of the crystallites. The failure of the grafted PFA samples to show a significant Fmoc loading was a result of the graft not being accessible under conditions of the loading tests. Thus, while the grafting of PFA with styrene using the preirradiation method in the presence of nitroxide did not provide an acceptable support for SPOC, the grafted copolymers may have promise as conducting membranes, for example. The rate of the grafting reaction was modified by the presence of a nitroxide and a uniform concentration of the styrene graft was obtained across the entire depth of the PFA lanterns.

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