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“Grafting-from” polymerization for uniformly bulk modification of pre-existing polymer materials via a supercritical-fluid route

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Abstract

A novel approach to uniformly bulk graft modification of pre-existing polymer materials without ungrafted homopolymers was achieved at relatively low temperature by means of gamma (γ)-rays pre-irradiation-induced “grafting-from” polymerization with supercritical carbon dioxide ($scCO_2$) both as solvent and as swelling agent. The polymer substrates were first irradiated with γ-rays originated from cobalt-60 resource under nitrogen atmosphere at ambient temperature, and thereby leading to uniform formation of trapped radicals on polymer backbone. Then, the produced polymer-trapped radicals were utilized to initiate graft polymerization of vinyl monomers dissolved in $scCO_2$ within polymer substrates. A combination of transmission electron microscopy, scanning electron microscopy and elemental analysis shows that side graft chains covalently bonded to polymer substrate backbone in nanometer scale are uniformly dispersed within polymer membranes with a thickness of 5 mm. Altering the experimental conditions can easily control the grafting yield with regard to side graft-chain length. This method can also be applied to various functional polymer chains covalently attached to different polymer substrates, even with high viscosity or limited solubility. The novel graft-polymer materials produced by this method are not formed in the absence of $scCO_2$ and are impossible to prepare by conventional methodologies.

Keywords: Supercritical CO_2; “Grafting-from” polymerization; Polymeric materials

1. Introduction

Chemical modification of pre-existing polymer materials by functional monomers has always been an object of great interest as it offers an effective route to address some low cost commodity shaped materials to higher added value applications [1–4]. Most of these studies have focused on surface modification by means of either “grafting-to” or “grafting-from” techniques [5–12]. “Grafting-to” involves the bonding of a preformed end-functionalized polymer chains to the reactive surface groups on the substrate. The limitation in this technique is that the attachment of a small number of chains significantly hinders diffusion of additional polymer chains to the surface, thereby leading to very low grafting density. In the grafting-from technique, initiator species on the substrate surface are used to initiate polymerization upon exposure to a monomer solution under appropriate conditions, so that high grafting density can be achieved. Usually, the formation of reactive species on a polymer substrate is carried out by several methods such as decomposition of chemical initiator, ultraviolet light radiation, plasma treatment and high energy radiation [12–14]. Among them, radiation-induced graft polymerization of pre-existing polymer materials is well known for its merits and potential in modifying the surface properties of pre-existing polymer materials without changing their inherent properties [2]. In sharp contrast to most focuses on surface modification, little attention has been paid to uniformly bulk graft modification of pre-existing polymer materials, which has great potential application in preparing impact-resistant plastics, thermoplastic elastomers, and polymer electrolyte membranes suitable for uses in fuel cells, batteries and sensors [15,16].

Recently, supercritical fluids (SCF), especially supercritical carbon dioxide ($scCO_2$), have unique mass transport properties, which are expected to provide a powerful means for the

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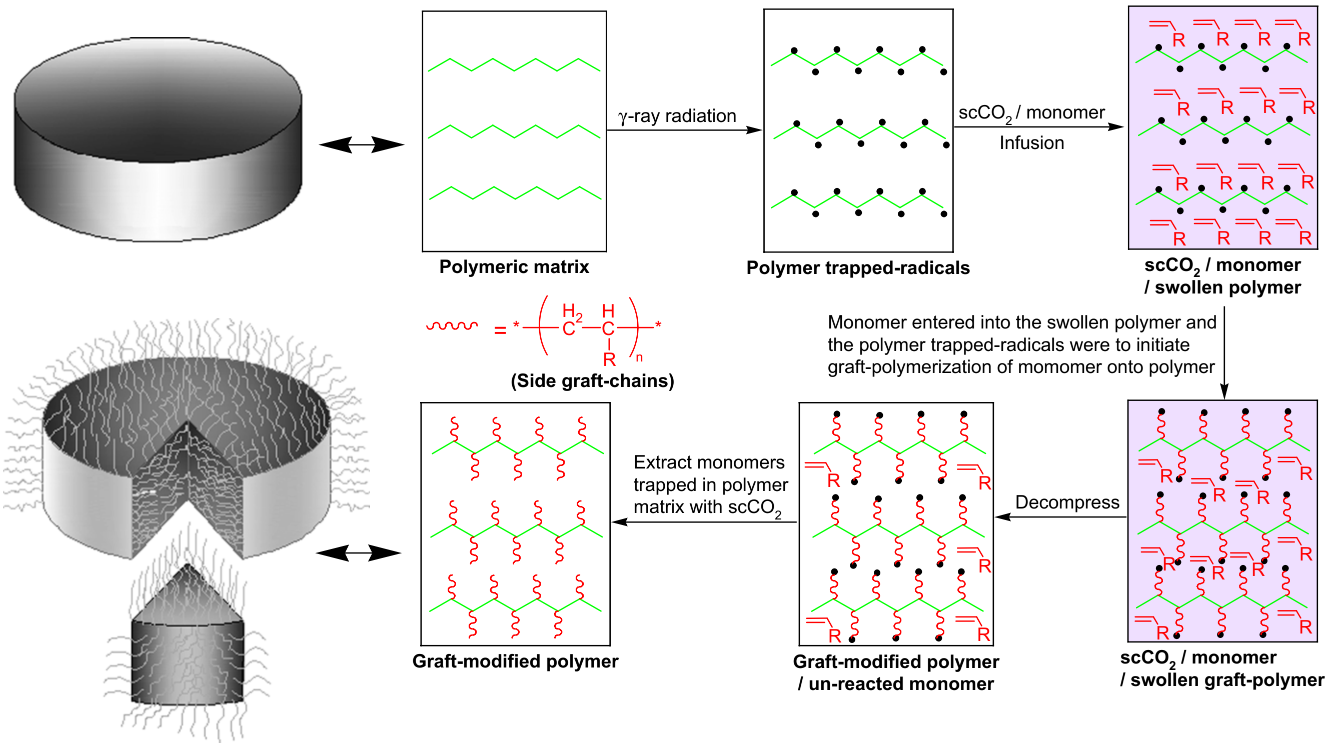

Fig. 1. Schematic representation of uniformly bulk graft modification of vinyl monomers to γ-rays activated pre-existing polymer materials with $scCO_2$ as both solvent and swelling agent.

development of polymer synthesis and polymer processing based on green chemistry [17,18]. Apart from their tunable physical properties and environmental advantages, the low viscosity of supercritical fluids and their ability to plasticize glassy polymers have implications on polymer processing [19−21]. In addition, the use of a low viscosity supercritical fluid as medium is beneficial to decrease solvent cage effects in free-radical initiator decompositions [22]. The unique properties associated with $scCO_2$ stimulated McCarthy and colleagues to develop an elegant method for preparing polymer blends with $scCO_2$ as a solvent [23−25]. Then, a number of blends of different polymers have been produced by this methodology [26−36]. The general procedure involved in the use of $scCO_2$ as both a swelling agent and a solvent for impregnating a CO_2-insoluble polymeric host with a mixture of monomers and an initiator. Polymerization is then initiated thermally (up to 120 °C) within the host polymer to form a blend, either in the presence of $scCO_2$ or after venting the CO_2 replacement with N_2. Unfortunately, no evidence of grafting was observed, and transmission electron microscopy (TEM) revealed that the formed polystyrene (PS) homopolymer existed as discrete phase-segregated regions throughout the thickness of the polymer substrates [24]. A attempt of gamma (γ)-rays radiation-induced maleation of polypropylene was carried out by charging maleic anhydride and dicumyl peroxide into polypropylene matrices using $scCO_2$ and then through γ-rays radiation at atmosphere of 0.1 MPa and 25 °C, but the homopolymers predominately formed and the grafting yield is very low [37].

Herein, we describe a green and versatile route to bulk graft modification of pre-existing polymer materials by means of "grafting-from" polymerization with $scCO_2$ both as solvent and as swelling agent (Fig. 1). Thus, the polymer substrate was first irradiated with γ-rays originated from cobalt-60 resource under nitrogen atmosphere at ambient temperature and then uniformly formed trapped radicals on polymer backbone, which can be stably existed ∼15 days at the low temperature of less than −25 °C. In the following step, the produced polymer-trapped radicals were utilized to initiate graft polymerization of vinyl monomers dissolved in $scCO_2$ within polymer substrates. Finally, the un-reacted monomers trapped in polymer matrix were further removed via $scCO_2$ extraction. Our strategy takes advantage of the fact that γ-ray has high penetration depth to various polymers and will lead to a uniform distribution of radical initiating sites on polymer backbone throughout the thickness of the irradiated samples. On the other hand, a key advantage of the use of $scCO_2$ is that the low viscosity of $scCO_2$ and its ability to plasticize glassy polymers are of benefit for the diffusion of vinyl monomers to the internal layers of pre-existing polymer materials [38−40]. In addition, the presence of CO_2 does not interfere with the chain-growth process during polymerization [41].

2. Experimental

2.1. Materials

Polypropylene (PP) (∼65% crystallinity) and low-density polyethylene (LDPE) without any additive were kindly provided by Liaoyang Petrochemical Corporation Ltd. Silicone rubber membrane was received from Dalian Plastic Factory and was washed twice with ethanol. PP and LDPE membranes with a thickness of 4–5 mm were prepared by melt-pressed film method at 180–230 °C. Styrene, methylmethacrylate (MMA), *N*-vinylpyrrolidone (*N*-VP) and 2-hydroxyethyl methacrylate (HEMA) were distilled under reduced pressure and stored at nitrogen atmosphere. Carbon dioxide (99.995%) was purchased from Dalian Institute of Special Gases and further purified by removing O_2 prior to use.

2.2. Representative graft-polymerization procedure

The grafting reaction was carried out in an autoclave of 60 mL as shown in Fig. 2. A representative procedure is described as follows: the weighed polymer samples were first treated under vacuum for 24 h and then filled with nitrogen gas. The samples were put into a glass ampoule at nitrogen atmosphere and irradiated in cobalt-60 resource of 1×10^5 Ci with a dose rate of 6 kGy/h for 10 h. After irradiation, the samples were rapidly stored at the low temperature of less than −25 °C prior to the grafting reaction. The irradiated samples were removed into the autoclave at nitrogen atmosphere, and then vinyl monomer (such as styrene) and liquid CO_2 were filled into it. Then, the autoclave was heated to 35 °C and maintained at the constant temperature and pressure. After a desired period, the un-reacted monomers together with CO_2 was removed from the autoclave, and then fresh CO_2 was put into it for extracting the un-reacted monomers trapped in polymeric substrate.

For a systematical comparison, the grafted samples (such as the styrene-grafted-PP) were further extracted by benzene or benzene/scCO_2 mixture for removing the possibly formed ungrafted polystyrene homopolymer. The samples were dried in an oven at 50 °C under vacuum and the grafting yield was calculated from the following equation:

$$\text{Grafting yield}\ (\%) = \left(W_g - W_0\right)/W_0 \times 100$$

where W_0 and W_g are the weights of the original and the grafted samples, respectively.

The grafting yield of inner (∼2.5 mm central region for the membranes of 5 mm thickness) or outer layer (surface region of 0.1 mm) of the styrene-grafted-PP samples was based on elemental analysis and calculated from the following equation:

$$\text{Grafting yield}\ (\%) = (C - 0.8562)/(0.9226 - C) \times 100$$

where C is the carbon content in the styrene-grafted-PP samples determined by elemental analysis; 0.8562 is mass fraction of carbon element in the original PP sample; 0.9226 is mass fraction of carbon element in the neat polystyrene.

Safety warning: the high-pressure equipment such as that required for these experiments should be equipped with a relief valve and/or (preferably) a rupture disk for minimizing the risk of personal injury.

2.3. Instrument and characterization

Differential scanning calorimetric (DSC) analyses of all resulted polymers were performed on NETZSCH DSC 204, with a heating rate of 10 K/min from 0 to 200 °C. The element components of the polymer membranes at various depths were determined in a Vario El III Element Analyzer. Scanning electron microscopic (SEM) experiments were performed using a KYKY-2800B SEM (KYKY Technology Development Co., China). The phase morphological characteristics of the grafted samples were observed by means of transmission electron microscopy (TEM) (Tecnai 20, FEI Co., USA). Prior to the examination, cryoultrathin films (in cross-section, Fig. 3) were cut using an ultramicrotome and they were chemically stained in OsO_4 vapor for 24 h.

3. Results and discussion

For the system of CO_2, styrene (as model vinyl monomer) and polymer, the fluid phase (CO_2–styrene mixture) is homogeneous under the experimental conditions (35–55 °C, 9.0–13.0 MPa), according to the reported phase behavior data for the CO_2–styrene system [25]. During the grafting process, the important role of CO_2 is its plasticizing effect on the polymer substrate, which results in the lowering of the polymer's glass transition temperature [38–40]. The monomer infuses the polymer substrate with the aid of scCO_2 until an equilibrium

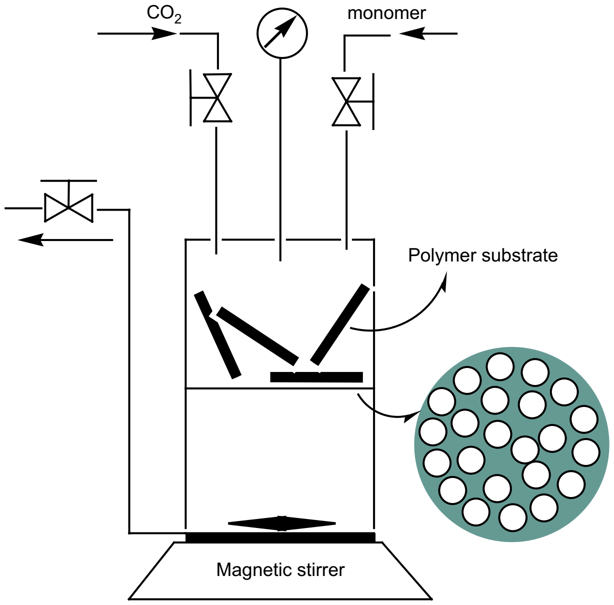

Fig. 2. Schematic view of the experimental instrument.

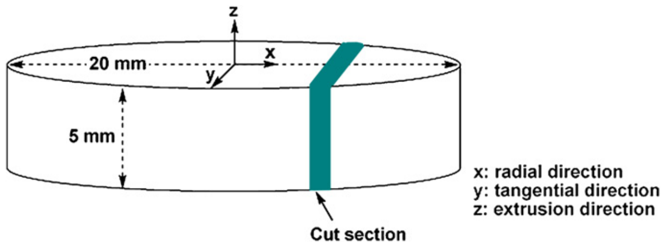

Fig. 3. Schematic diagram showing the microtoming of the grafted samples.

Table 1
Free-radical polymerization of styrene from various γ-rays' activated polymer membranes of 5 mm thickness[a]

Run	Polymer substrate	Styrene concen. (mol/L)	Temp. (°C)	Time (h)	Grafting yield (%)		
					Average	Inner layer[b]	Outer layer[b]
1	PP	0.29	35	12	15.0	13.5	14.8
2	PP	0.68	35	12	25.4	21.6	26.5
3	PP	0.68	35	24	35.6	32.5	36.8
4	PP	1.44	35	12	33.8	23.7	46.2
5	PP	0.68	55	12	32.9	29.6	35.1
6	PP	0.68	55	24	55.1	57.7	53.2
7[c]	PP	2.16	35	24	19.9	0	240.8
8	LDPE	0.29	35	12	16.1	16.9	15.8
9	SR[d]	0.29	35	12	18.3	18.4	18.9
10	SR	1.44	35	12	40.1	38.5	40.7

[a] Reactions were carried out in an autoclave of 60 mL at 9.0–13.0 MPa. Prior to the grafting reaction, the samples were irradiated in a total dose of 60 kGy with a dose rate of 6 kGy/h.

[b] The experiment was repeated for 3–5 times and an average value was obtained on the basis of elemental analysis.

[c] Reaction was carried out in a glass ampoule at nitrogen atmosphere with methanol as solvent along with the formation of ungrafted polystyrene homopolymer of up to 22.5% with regard to polymer substrate.

[d] Silicone rubber.

of the monomer distributing between the polymer substrate and the CO_2-rich fluid phase is reached. The equilibrium time should depend on the properties of the fluid phase, the solid polymer and reactive radical species.

Usually, radiation-induced graft copolymerization of pre-existing polymeric materials is usually carried out in organic solvent with high vinyl monomer concentration [42,43]. We delightfully found that the present method was proved to be effective in the bulk graft modification of styrene to polypropylene (PP, ∼65% crystallinity), low-density polyethylene (LDPE) and silicone rubber (SR) membrane with a thickness of 5 mm, even with very low monomer concentration of 0.29 mol/L (Table 1, runs 1, 8 and 9). Of importance, approach to homogeneously and uniformly bulk graft modification was observed throughout the thickness of the polymer substrates by means of elemental analysis. It is worth noting that the increased mass is completely resulted from grafting chain, because no observable loss in weight was found in the resulted products after further extraction with benzene or benzene/$scCO_2$ mixture for 24 h. These results are in sharp contrast to that of the system with the substitution of methanol for $scCO_2$ as solvent, grafting predominately takes place in the surface of the polymer substrate, along with the formation of ungrafted polystyrene homopolymer of up to 53% of the increased mass (Table 1, run 7). Notably, the grafting process was carried out at relatively low temperature, and thereby completely avoiding thermal stresses, which is very advantageous for bulk graft modification of thermo-sensitive materials.

The distribution of the side polystyrene graft chains inside PP matrix was investigated by measuring carbon content of a cross-section of the graft-modified sample (Fig. 4). A typical curve is shown in Fig. 4a, which marks a uniform type of distribution, in contrast to polymer surface modification with methanol as solvent (Fig. 4b). The results clearly indicate that CO_2 acts as a low molecular plasticizer that enhances the mobility of styrene inside the polymeric matrix. Indeed, in γ-rays radiation-induced grafting process performed in organic solvent, though the addition of good-swelling diluents is of benefit for the diffusion of monomers to the internal layers of polymer substrates and thus likely results in bulk grafting in some cases, the high viscosity in graft region will easily cause polymer radicals' transfer to monomers or solvents and thus predominately produce ungrafted homopolymers rather than graft polymers. Also, the high viscosity resulting from side graft chains and ungrafted homopolymers significantly hinders diffusion of monomers to the inner layers of polymer matrix, thereby leading to low grafting yield and unexpected heterogeneous grafting. Furthermore, the complete removal of organic swelling reagent, un-reacted trapped monomers and concomitant ungrafted homopolymers from the modified polymer matrix is extremely difficult [44,45].

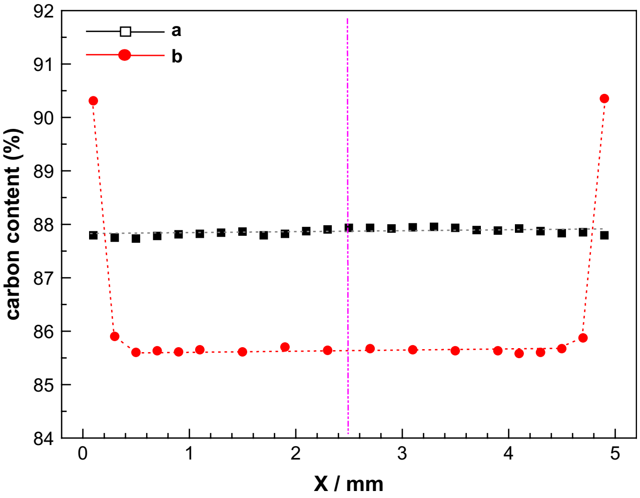

Fig. 4. Carbon distribution of the styrene-grafted-PP samples with a thickness of 5 mm at various depths (a) using $scCO_2$ as solvent (grafting yield: 55.1%) and (b) using methanol as solvent (grafting yield: 19.9%).

For further confirming the uniformly bulk grafting property, the modified sample was microtomed in cross-section so that the distribution of side polystyrene graft chains from the surface to the center of the sample could be examined. Fig. 5 displays transmission electron microscopic (TEM) micrograph of a styrene-grafted PP sample in cross-section, in which the dark phase results from the OsO_4-stained polystyrene graft chains. As expected, the side polystyrene graft chains are uniformly dispersed in the PP matrix and the graft-chain size is about 50 nm throughout the thickness of the modified sample. Differential scanning calorimetric (DSC) measurements were carried out for irradiated PP, irradiated PP processed with neat $scCO_2$ at 35 °C and 10 MPa for 8 h, and a styrene-grafted-PP sample with grafting yield of 23.1% (Fig. 6). It can be seen that the properties of the $scCO_2$-treated and untreated PP samples are nearly the same. The grafting of styrene to PP reduces the heat of fusion associated with crystallinity, but the crystallinity of the PP portion of the grafting sample

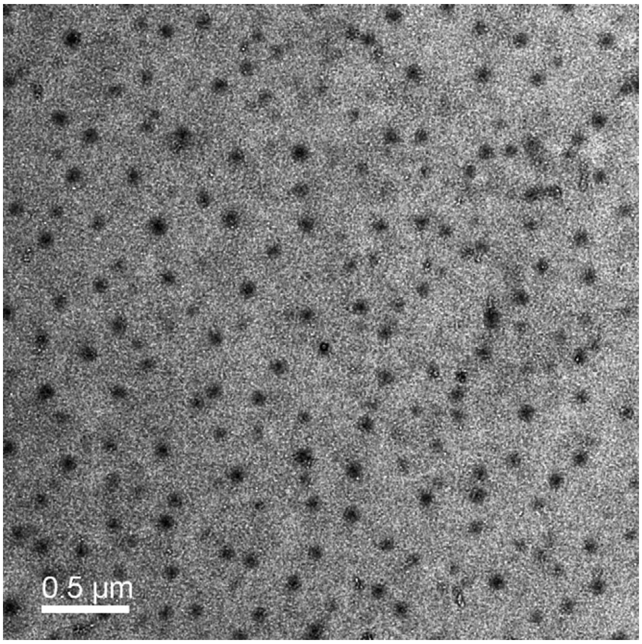

Fig. 5. TEM micrograph (cross-section) of a styrene-grafted-PP sample (grafting yield: 31.0%).

almost remains unchanged, mainly because the graft predominately occurs in amorphous part of the PP substrate. Indeed, after irradiation, the polymer-trapped radicals are formed and distributed in the crystalline region and amorphous region of polymer materials. The life of the radicals is very short in amorphous region, which will form the peroxide in the presence of oxygen [46]. But those radicals trapped in crystalline region have long life at low temperature and will move into the interface of crystalline region and amorphous region to initiate grafting reaction at certain condition, the graft predominately occurs in amorphous part of the polymer substrate.

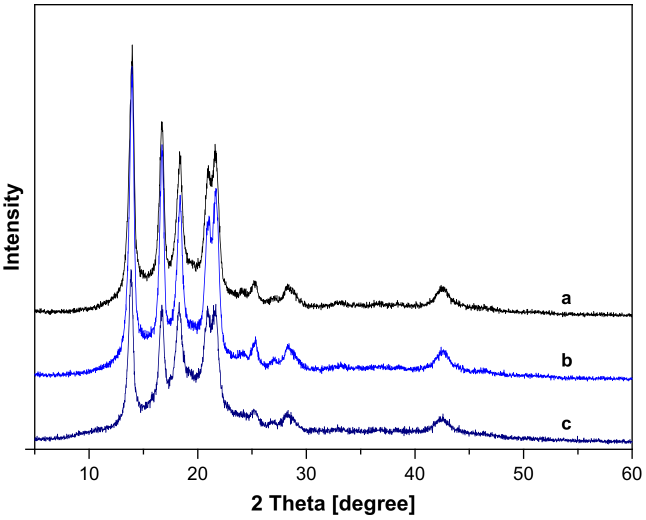

Fig. 7. XRD spectra of (a) original PP (b) irradiated PP, and (c) the styrene-grafted-PP sample with a grafting yield of 46.9%.

Although a significant decrease in intensity of diffraction peaks was found in the styrene-grafted PP membrane (Fig. 7c) due to the presence of the amorphous side graft chains on polymer substrate as compared with the original or irradiated PP samples (Fig. 7a and b), the ratio of the total integrating area of diffraction peaks resulting from crystalline region versus that of diffuse reflection from non-crystalline region did not show obvious change before and after grafting.

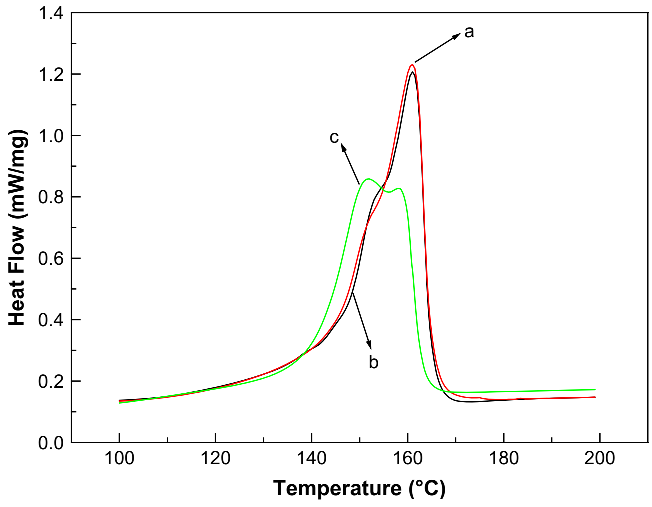

Fig. 6. DSC thermographs (heating) for (a) irradiated PP, (b) irradiated PP processed with neat scCO$_2$ at 35 °C and 10 MPa for 8 h, and (c) the styrene-grafted-PP sample with a grafting yield of 23.1%.

Table 1 also shows the strong influence of monomer concentration. An increase in the styrene concentration between 0.29 and 1.44 mol/L results in a dramatic increase in grafting yield. Interestingly, the increase of styrene concentration in PP systems leads to an unexpected gradient bulk graft modification (a decrease of grafting yield from the outer to inner layer, run 4), but in amorphous polymers such as SR system the variation of monomer concentration has a slight effect on their uniformly bulk grafting modification (run 10). This may originate from the stronger swelling ability of scCO$_2$ to the glassy polymers than the crystallizing PP. A change in the reaction temperature from 35 to 55 °C is beneficial to uniformly bulk graft modification of PP, and also causes an increase in grafting yield (run 5). Since grafting is a diffusion-controlled process, the enhancement of temperature benefits monomer

Table 2
Free-radical polymerization of functional vinyl monomers from various γ-rays' activated polymer membranes of 5 mm thickness[a]

Run	Polymer substrate	Vinyl monomer	Monomer concen. (mol/L)	Temp. (°C)	Grafting yield[b] (%)		
					Average	Inner layer	Outer layer
1	PP	HEMA	0.27	55	30.6	26.6	33.2
2	PP	*N*-VP	0.78	55	36.2	31.5	38.1
3	PP	MMA	0.95	35	21.7	15.3	29.5
4	LDPE	*N*-VP	0.78	55	23.3	21.4	26.2
5	LDPE	MMA	0.95	35	25.1	19.4	29.9
6	SR	*N*-VP	0.78	55	18.9	19.1	18.9
7	SR	MMA	0.95	35	17.8	16.2	18.1

[a] Reaction was carried out in an autoclave of 60 mL for 12 h at 9.0–13.0 MPa, the samples were irradiated in a total dose of 60 kGy with a dose rate of 6 kGy/h.

[b] The experiment was repeated for 3–5 times and an average value was obtained on the basis of elemental analysis, in conjunction with FTIR analysis.

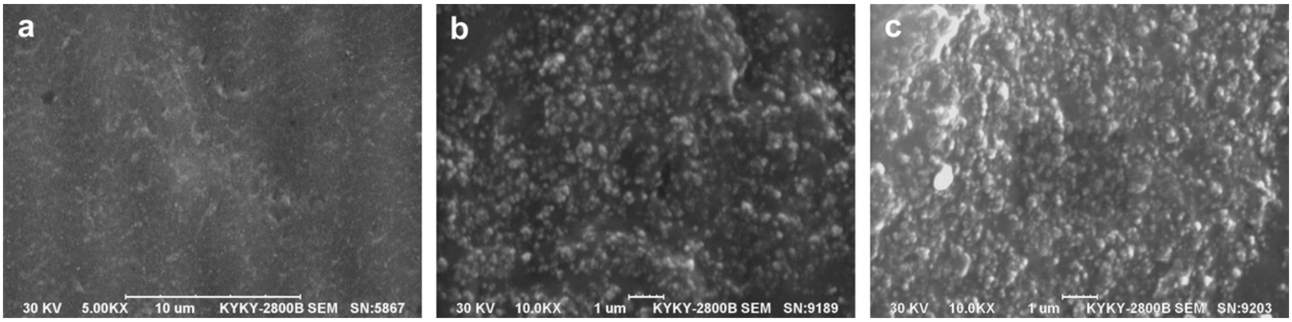

Fig. 8. SEM photographs (cross-section) of (a) original silicon rubber (SR), (b) the MMA grafted SR sample with a grafting yield of 31.2%, and (c) the HEMA grafted SR sample with a grafting yield of 38.5%.

diffusion into the polymer matrix leading to the presence of sufficient monomer units in grafting zone. Indeed, in pre-irradiation-induced graft polymerization, the initial rate of grafting with respect to the reactivity of polymer-trapped radicals increases with the enhancement of the reaction temperature, but the grafting rate decreases with the increase of time because of the growing chains' radical–radical termination. It is noteworthy mentioning that the increase of reaction time also trends to uniformly bulk graft modification for PP system. We tentatively assume that the lifetime of polymer-trapped radicals or growing chain radicals is in inverse proportion to their grafting chain length.

Furthermore, the present method was also succeeded in applying to bulk graft modification of functional vinyl monomers such as *N*-vinylpyrrolidone (*N*-VP), methylmethacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) to various polymer substrates (Table 2). The bulk grafting is confirmed by element determinant and FTIR analyses for comparing characteristic peak intensity of side graft chain of the grafted samples at outer and inner layers (not shown), as well as scanning electron microscopic (SEM) observation of the cross-section of the samples. Fig. 8 displays SEM micrographs of cross-section surfaces of the original SR, the MMA and HEMA grafted SR samples. The morphologies of the grafted samples (Fig. 8b and c) are significantly different from that of the original sample (Fig. 8a). The cross-section surface shows a uniformly dispersed graft-chain phase in the range 100–200 nm throughout the thickness of the modified samples, while the original sample is very flat.

Table 3
Mechanical properties of various polymer membranes and their bulk grafting samples[a]

Run	Polymer	Grafting yield (%)	Strain at break (MPa)	Elongation at break (%)
1	LDPE		13.3	708
2	Irradiated LDPE		13.3	653
3	LDPE-g-P$_{st}$	18.1	6.5	319
4	LDPE-g-P$_{st}$	46.9	13.2	35
5	LDPE-g-P$_{N\text{-VP}}$	4.3	13.1	651
6	LDPE-g-P$_{\text{HEMA}}$	6.2	16.0	703
7	LDPE-g-P$_{\text{MMA}}$	4.8	8.4	264
8	SR		3.0	419
9	Irradiated SR		1.9	214
10	SR-g-P$_{\text{HEMA}}$	3.7	2.8	261
11	SR-g-P$_{\text{MMA}}$	13.3	2.6	261
12	PP		20.1	430
13	PP-g-P$_{st}$	15.7	9.9	105

[a] Reaction was carried out in an autoclave of 200 mL for 12–24 h at 35–55 °C and 9.0–13.0 MPa. The samples were irradiated in a total dose of 20 kGy with a dose rate of 2 kGy/h. The measurement was repeated for 3–5 times.

It is generally known that high energy radiation probably leads to the molecular change in polymers, such as chain crosslinking or scission. Chain crosslinking causes an increase in the molecular weight and forms a microscopic network structure, while chain scission results in a decrease in the molecular weight and substantially alters the polymeric material properties. The extent of chain crosslinking or scission depends on the chemical nature of the polymer and irradiation conditions, i.e., irradiation dose and dose rate. Under radiation condition of a total dose of 20 kGy with a dose rate of 2 kGy/h, LDPE membranes did not exhibit an observable change in the elongation at break and the strain at break before and after grafting (Table 3, runs 1 and 2), but a significant decrease was found in the SR samples (runs 8 and 9). The presence of side polystyrene graft chains substantially reduced the elongation at break. The grafting yield increasing from 18.1 to 46.9% for the styrene-grafted-LDPE samples resulted in the elongation at break decreasing from 319 to 35%. Interestingly, the elongation at break and the strain at break of the *N*-VP or HEMA grafted samples with a low grafting yield are close to that of the original polymer. It is worth noting that the low grafting yield of less than 10% usually causes slight change in the shape of the pre-existing polymer materials. A detailed investigation on optimal experimental conditions and further application of this method for preparing ion exchange membranes are in progress.

4. Conclusions

In summary, we report a strategy for homogeneously and uniformly bulk graft modification of pre-existing polymer materials by means of γ-rays radiation-induced "grafting-from" polymerization, in connection with the use of $scCO_2$ both as solvent and as swelling agent. The process parameters can be controlled by the experimental conditions. In sharp contrast to pre-irradiation-induced graft modification in organic solvent, the grafting process did not accompany with the formation of ungrafted homopolymers, indicating its advantages in synthesizing functional materials for medical purpose. In addition, the present method completely avoids thermal stresses and substantially broadens the application potential for radiation chemistry as it allows for the use of environmentally benign CO_2 to replace conventional organic solvents in many systems. Moreover, it also firstly demonstrates the feasibility of bulk graft modification of shaped polymer materials with high viscosity or limited solubility. We believe that this methodology can be extended to provide a very simple green route to a wide range of graft block copolymers by incorporating various vinyl monomers with very different physical and chemical properties, which is of benefit for preparing impact-resistant plastics, thermoplastic elastomers, and polymer electrolyte membranes suitable for uses in fuel cells, batteries and sensors.

Acknowledgments

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References

[1] Tsujii Y, Ohno K, Yamamoto S, Goto A, Fukuda T. Adv Polym Sci 2006;197:1.
[2] Nasef MM, Hegazy EA. Prog Polym Sci 2004;29:499.
[3] Jenkins DW, Hudson SM. Chem Rev 2001;101:3245.
[4] Klee D, Hocker H. Adv Polym Sci 1999;149:1.
[5] Mansky P, Liu Y, Huang E, Russell TP, Hawker CJ. Science 1997; 275:1458.
[6] Geng Y, Discher DE, Justynska J, Schlaad H. Angew Chem Int Ed 2006; 45:7578.
[7] Joester D, Klein E, Geiger B, Addadi L. J Am Chem Soc 2006;128:1119.
[8] Choi WS, Park JH, Koo HY, Kim JY, Cho BK, Kim DY. Angew Chem Int Ed 2005;44:1096.
[9] Ulbricht M, Yang H. Chem Mater 2005;17:2622.
[10] Parrish B, Breitenkamp RB, Emrick T. J Am Chem Soc 2005;127: 7404.
[11] Buga K, Majkowska A, Pokrop R, Zagorska M, Djurado D, Pron A, et al. Chem Mater 2005;17:5754.
[12] Brack HP, Padeste C, Slaski M, Alkan S, Solak HH. J Am Chem Soc 2004;126:1004.
[13] Xu Z, Wang J, Shen L, Men D, Xu Y. J Membr Sci 2002;196:221.
[14] Choi YJ, Kang MS, Kim SH, Cho J, Moon SH. J Membr Sci 2003; 223:201.
[15] De Rosa C, Auriemma F. Adv Mater 2005;17:1503.
[16] Yamazaki S, Ioroi T, Yamada Y, Yasuda K, Kobayashi T. Angew Chem Int Ed 2006;45:3120.
[17] Kendall JL, Canelas DA, Young JL, Desimone JM. Chem Rev 1999; 99:543.
[18] Cooper AI. Adv Mater 2003;15:1049.
[19] Bungert B, Sadowski G, Arlt W. Ind Eng Chem Res 1998;37:3208.
[20] Hebb AK, Senoo K, Bhat R, Cooper AI. Chem Mater 2003;15:2061.
[21] Duxbury CJ, Wang W, de Geus M, Heise A, Howdle SM. J Am Chem Soc 2005;127:2384.
[22] Guan Z, Combes JR, Menceloglu YZ, Desimone JM. Macromolecules 1993;26:2663.
[23] Watkins JJ, McCarthy TJ. Macromolecules 1994;27:4845.
[24] Watkins JJ, McCarthy TJ. Macromolecules 1995;28:4067.
[25] Suppes GJ, McHugh MA. J Chem Eng Data 1989;34:310.
[26] Li D, Han B. Macromolecules 2000;33:4555.
[27] Li D, Han B. Ind Eng Chem Res 2000;39:4506.
[28] Muth O, Hirth T, Vogel H. J Supercrit Fluids 2000;17:65.
[29] Friedmann G, Guilbert Y, Catala JM. Eur Polym J 2000;36:13.
[30] Li D, Han B, Liu ZM. Macromol Rapid Commun 2001;202:2187.
[31] Li D, Liu Z, Han B, Song L, Yang G, Jiang T. Polymer 2002;43:5363.
[32] Liu Z, Dong Z, Han B, Wang J, He J, Yang G. Chem Mater 2002;14:4619.
[33] Zhang JX, Busby AJ, Roberts CJ, Chen XY, Davies MC, Tendler SJB, et al. Macromolecules 2002;35:8869.
[34] Busby AJ, Zhang J, Naylor A, Roberts CJ, Davies MC, Tendler SJB, et al. J Mater Chem 2003;13:2838.
[35] Wang Y, Liu Z, Han B, Dong Z, Wang J, Sun D, et al. Polymer 2004;45:855.
[36] Naylor A, Howdle SM. J Mater Chem 2005;15:5037.
[37] Spadaro G, De Gregorio R, Galia A, Valenza A, Filardo G. Polymer 2000;41:3491.
[38] Wissinger RG, Paulaitis ME. J Polym Sci Part B Polym Phys 1987; 25:2497.
[39] Goel SK, Beckman EJ. Polymer 1993;34:1410.
[40] Condo PD, Paul DR, Johnston KP. Macromolecules 1994;27:365.
[41] Van Herk AM, Manders BG, Canelas DA, Quadir M, Desimone JM. Macromolecules 1997;30:4780.
[42] Gupta B, Chapiro A. Eur Polym J 1989;25:1137.
[43] Fang Y, Ma C, Chen Q, Lu X. J Appl Polym Sci 1998;68:1745.
[44] Cardona F, George GA, Hill DJT, Rasoul F, Maeji J. Macromolecules 2002;35:355.
[45] Dargaville T, George G, Hill D, Whittaker A. Prog Polym Sci 2003; 28:1355.
[46] Wang YM, Pan Y, Wang YL, Wu GP, Wang YJ, Nikitin LN, et al. J Supercrit Fluids 2007; doi:10.1016/j.superflu.2007.09.018.