

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



A Novel Grafting of Polymers onto the Surface of Graphene Oxide

Norio Tsubokawa, Takeshi Yamauchi,
Kazuhiro Fujiki and Shingo Tamesue

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67477>

Abstract

A simple grafting of polymers onto graphene oxide (GO) was achieved by polymer radical trapping, ligand-exchange reaction, and surface initiated cationic and anionic graft polymerization. Grafting of poly(ethylene glycol) (PEG) onto GO was successfully achieved by trapping of PEG radicals formed by thermal decomposition of PEG macroazo initiator to give PEG-grafted GO. The grafting of copolymers containing vinyl ferrocene moieties onto GO surfaces was also successfully achieved by the ligand-exchange reaction between ferrocene moieties of these copolymers and GO. Carboxyl groups on GO have an ability to initiate the cationic polymerizations of vinyl monomers, such as *N*-vinylcarbazole and isobutyl vinyl ether. The corresponding vinyl polymers were grafted onto GO, during the cationic polymerization, based on the termination of growing polymer cation by counter anion (carboxylate) groups on GO. It was found that the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides was successfully initiated by potassium carboxylate groups on GO, introduced by neutralization of carboxyl groups with KOH, to give the corresponding polyester-grafted GO. The dispersibility of GO in organic solvents was remarkably improved by the grafting of the above polymers onto GO. In addition, easy preparation of reduced GO-based conducting polyaniline composite organogel will be discussed.

Keywords: graphene, graphene oxide, grafting of polymers, surface-initiated polymerization, ligand-exchange reaction

1. Introduction

Recently, graphene and graphene oxide (GO), as well as carbon nanotube, nanodiamond, and fullerene, have emerged as excellent nanomaterials having electrical and thermal conductive,

mechanical, gas barrier, optical, and antibacterial properties. Therefore, a polymer composite with GO has recently attracted much interest in the materials field due to its outstanding properties [1–8]. Especially, many researchers have reported the preparation and properties of GO/chitin and GO/biopolymer composites [9–15]. For example, Travlou et al. have reported the synthesis and applications of GO/chitosan and GO/polysaccharides nanocomposites [9, 14].

It is well known that in comparison with GO/chitin nanocomposite, we can obtain GO having an excellent dispersibility into organic solvents and various polymer matrices by grafting of conventional polymers onto GO and readily obtain thermosetting, thermoplastic, and thermo-elastic polymer nanocomposite thin films having electro and thermal conductivity. The surface modifications of graphene oxide (GO) by grafting of polymers via atom transfer radical polymerization (ATRP) [4–6, 16, 17] and reverse addition fragmentation chain transfer polymerization (RAFT) have been reported by many researchers [7, 8, 18]. According to the above-mentioned method, polymer brush grafted onto GO can be obtained.

However, the above graft polymerization needs the complicated treatment for the introduction of surface-initiating groups. Therefore, it is desired to develop a simple and an easy method for the grafting of polymers onto GO without complicated procedures for the introduction of the initiating groups onto GO.

On the other hand, we have also achieved the grafting of various polymers onto various nanocarbons such as carbon black, carbon nanotubes, fullerene, and nanodiamond, by “grafting from” and “grafting onto” methods [19, 20]. We have designed a simple surface grafting of various polymers onto these nanocarbons by polymer radical trapping [21, 22], ligand-exchange reaction [23, 24], surface-initiated cationic [25], and anionic graft polymerization [26]. According to the above processes, they do not require complicated process for the introduction of initiating groups onto nanocarbons for the graft polymerization.

In this chapter, a novel and an easy grafting of polymers onto GO without complicated pretreatment by trapping of polymer radicals [27], ligand-exchange reaction of ferrocene-containing polymer with GO [27], and simple cationic and anionic graft polymerization initiated by carboxyl groups on GO [28] are reviewed. In addition, the dispersibility of various polymer-grafted GO in several organic solvents and easy preparation of conductive composite gel consisting of reduced GO and polyaniline will be discussed.

2. Grafting of polymers onto GO by polymer radical trapping

2.1. Radical reactivity against aromatic compounds and nanocarbons

It has been reported that reactivity of methyl radical to aromatic compounds increases with the increasing number of aromatic rings: the relative reactivity of methyl radical against to carbon black is ten million times of that of benzene [29]. Therefore, nanocarbons, such as carbon black, fullerene, and carbon nanotube, are known as a strong radical-trapping agent.

It is well known that radical polymerization of vinyl monomers is dramatically retarded (or inhibited) in the presence of nanocarbons, such as carbon black and carbon nanotubes.

These results indicate that during the radical polymerization in the presence of nanocarbons, initiator radicals and growing polymer radicals are readily trapped by nanocarbons [29].

2.2. Confirmation of radical trapping ability of GO

To make sure the radical trapping activity of GO, the effect of GO on thermally initiated radical polymerization of styrene (St) at 80°C was investigated. **Figure 1** shows the result of the thermally initiated radical polymerization of St in the absence (blank) and in the presence of GO at 80°C.

As shown in **Figure 1**, it is found that the thermal radical polymerization of St is remarkably retarded in the presence of GO. It was confirmed that during polymerization, a part of polySt formed was grafted onto GO to give polySt-grafted GO (GO-g-polySt), although the formation of ungrafted polySt preferentially proceeded: the grafting of polySt onto GO was confirmed by GC-MS: the percentage of polySt grafting was less than few percentage. Based on the above results, it is concluded that GO has a strong radical-trapping activity.

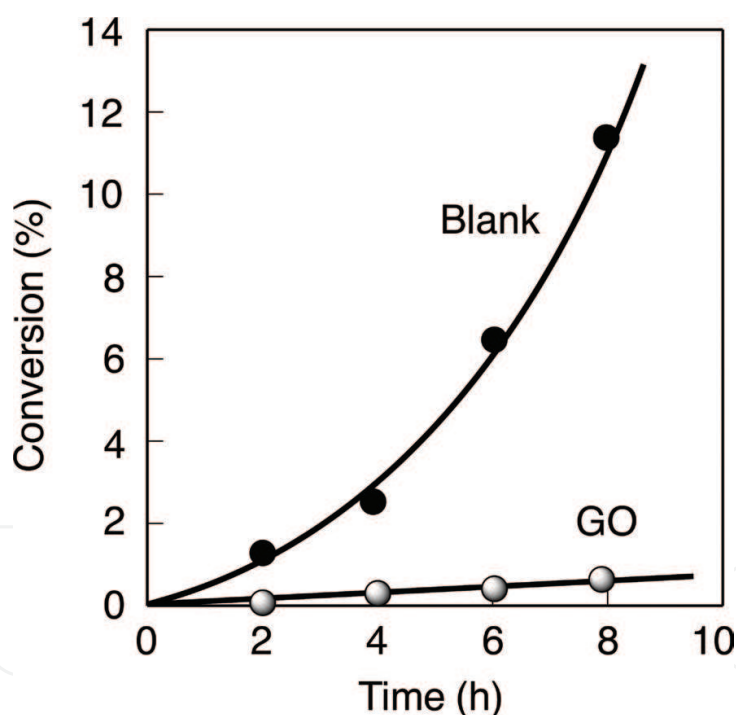
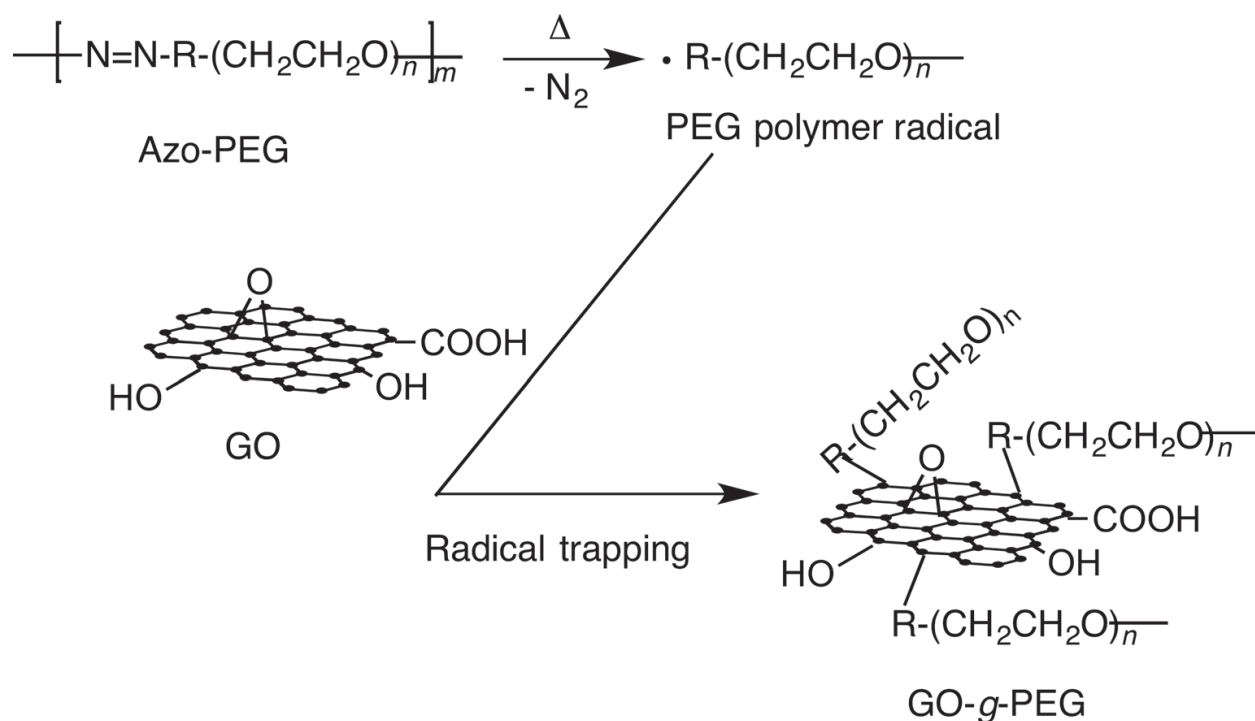


Figure 1. Thermally initiated radical polymerization of St in the absence (blank) and in the presence of GO (GO). GO, 0.10 g; St, 10.0 mL; Temp., 80°C.

2.3. Grafting of PEG by radical trapping

The grafting of poly(ethylene glycol) (PEG) onto the GO surface by trapping of PEG radicals produced by the thermal decomposition of PEG macroazo initiator (Azo-PEG) was investigated (**Scheme 1**). We used commercially available Azo-PEG [30].



Scheme 1. Grafting of PEG onto GO by the trapping of PEG radicals formed by thermal decomposition of Azo-PEG.

Figure 2 shows the effect of polymerization time on the percentage of PEG grafting (percentage of grafted polymer on GO) onto the GO surface. It is found that the percentage of PEG grafting increased with the passage of the polymerization and reached over 15% after 24 h.

The grafting of PEG onto GO, on the contrary, was hardly observed when GO was reacted at room temperature, because of no decomposition of Azo-PEG for the generation of PEG radicals.

2.4. Identification of PEG grafting onto GO by GC-MS

Identification of PEG grafting onto GO was achieved by using gas chromatogram and mass spectra (GC-MS) of thermally decomposed gas of GO-g-PEG. The GC-MS of PEG, GO-g-PEG, and untreated GO is shown in **Figures 3** and **4**. **Figure 3** clearly shows that the GC of GO-g-PEG agreed with that of PEG.

Furthermore, as shown in **Figure 4**, the MS of thermally decomposed gas of GO-g-PEG at retention time 6.8 min was also in accord with that of PEG: the structures of fragment at 45, 59, 73, and 89 (m/z) estimated from MS database are shown in **Figure 4**.

The MS of thermally decomposed gas of GO-g-PEG at other retention time was also in accord with that of PEG. These results suggested that PEG radicals, formed by the thermal

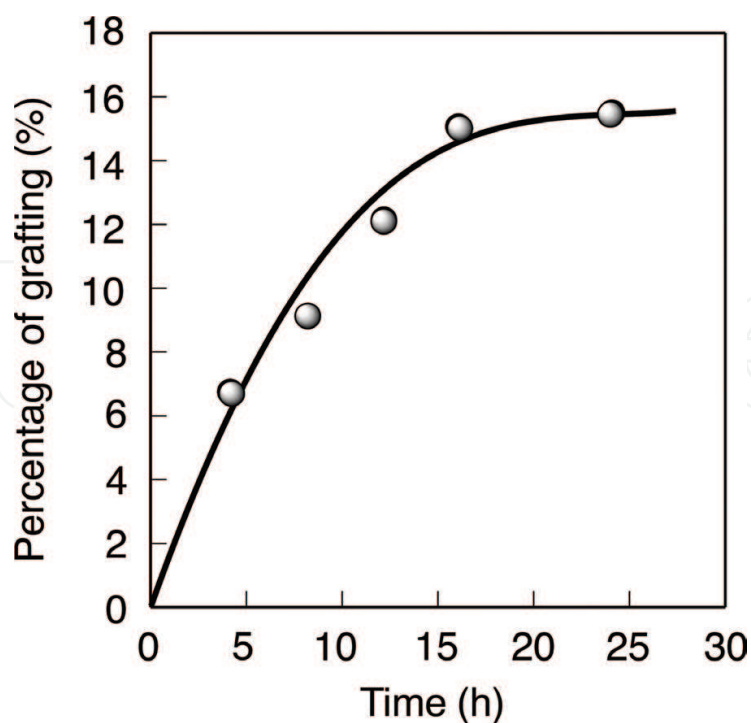
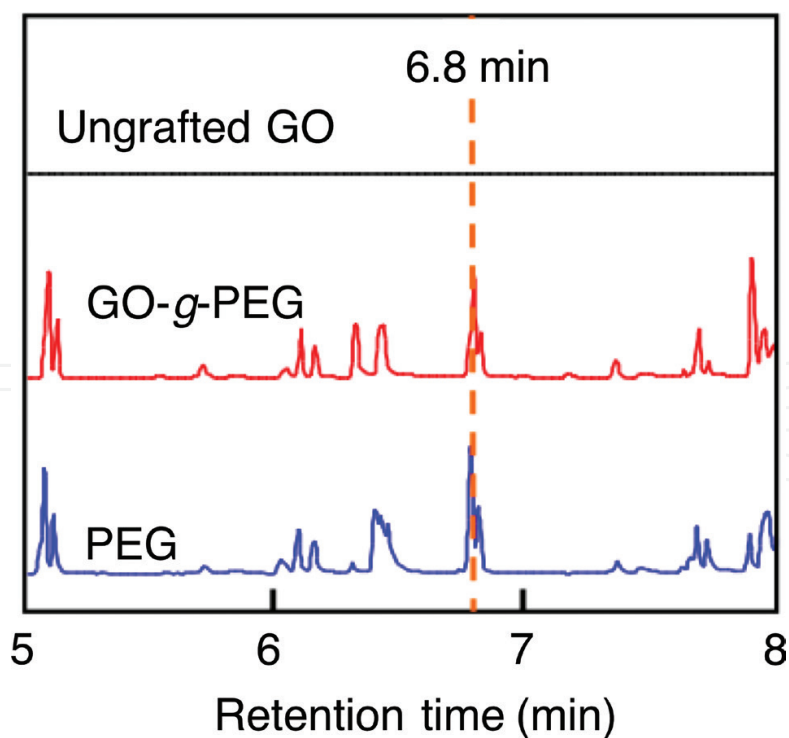


Figure 2. Grafting of PEG onto GO by the reaction of PEG with Azo-PEG. GO, 0.10 g; Azo-PEG, 2.00 g; toluene, 20.0 mL; Temp., 80°C.



Figures 3. Thermal decomposition gas chromatograms of untreated GO, GO-g-PEG, and PEG.

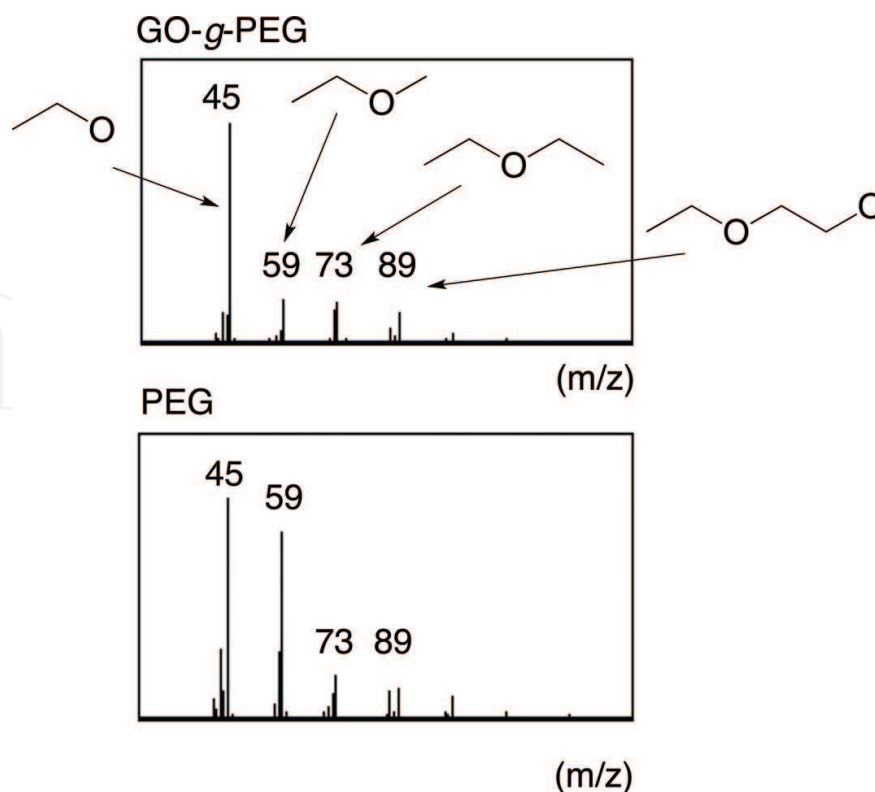


Figure 4. Mass spectra of decomposed gas of GO-g-PEG and PEG at retention time 6.8 min.

decomposition of Azo-PEG, are successfully captured by GO surface, and PEG is grafted (chemically bonded) onto GO.

3. Grafting of polymers onto GO by ligand-exchange reaction with ferrocene

3.1. Ligand-exchange reaction of ferrocene with graphene structure of nanocarbons

Morrison et al. reported that the h^6 -benzene- h^5 -cyclopentadienyliron cation could be readily prepared by the ligand-exchange reaction of ferrocene with benzene in the presence of AlCl_3 and Al powders as the catalysts [31, 32]. Furthermore, Miyake et al. reported that the ligand-exchange reaction is successfully applied for the introduction of functional groups to graphene structure of various carbon materials [32]. We have reported the grafting of polymers by ligand-exchange reaction of ferrocene moieties of polymers with graphene structure of carbon black, carbon fiber, and carbon nanofibers [23, 24]. Therefore, we designed the grafting of poly(Vf-co-MMA) onto GO surfaces by ligand-exchange reaction between ferrocene moieties of poly(Vf-co-MMA) and polycondensed aromatic rings of the GO surface, as shown in **Scheme 2**.

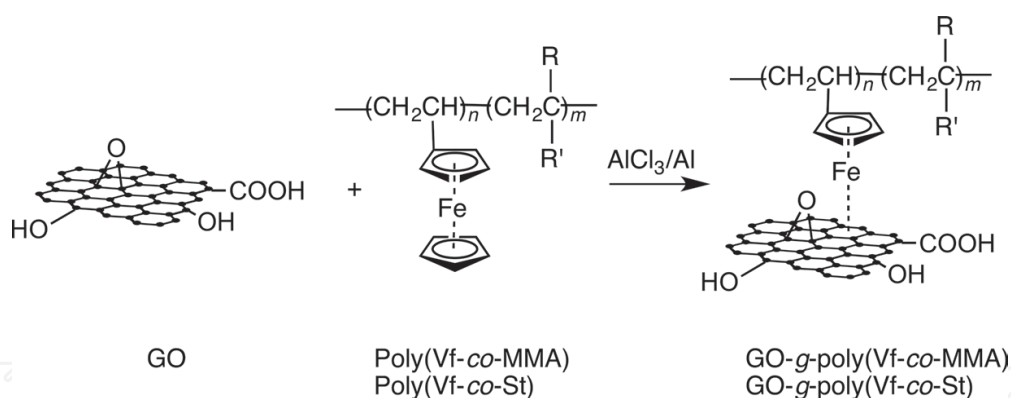
3.2. Preparation of poly(Vf-co-vinyl monomer) and characterization

Ferrocene containing copolymer of vinyl ferrocene (Vf) with methyl methacrylate (MMA) [poly(Vf-co-MMA)] and styrene (St) [poly(Vf-co-St)] was prepared by the copolymerization of the corresponding monomers, using 4,4'-azobisisobutyronitrile (AIBN) as an initiator.

Table 1 shows the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n), which are determined by SEC, Vf contents of poly(Vf-co-MMA), and poly(Vf-co-St), which are determined by elemental analysis, and are also shown in **Table 1**. As shown in **Table 1**, it is found that M_w/M_n of these copolymers prepared by the conventional radical copolymerization by using AIBN as an initiator is considerably narrow. The content of vinyl ferrocene (Vf) moieties of poly(Vf-co-MMA) and poly(Vf-co-St) is estimated to be 9.3 and 6.3%, respectively. $^1\text{H-NMR}$ and FT-IR are used to confirm the structures of poly(Vf-co-MMA) and poly(Vf-co-St).

3.3. Grafting of poly(Vf-co-MMA) and poly(Vf-co-St) onto GO by ligand-exchange reaction

The results of the grafting reaction of poly(Vf-co-MMA) with GO surface under several conditions are shown in **Table 2**. No grafting of the copolymer onto GO surface was hardly observed, even if, GO was reacted (heated) with poly(Vf-co-MMA) in 1,4dioxane in the absence of AlCl_3 and Al powders as a catalyst at 80°C for 24 h (Run 1). In addition, no grafting of the copolymer onto GO proceeded in the presence of Al powder alone (Run 2).



Scheme 2. Grafting of poly(Vf-co-MMA) and poly(Vf-co-St) onto GO by ligand-exchange reaction of these copolymers with polycondensed aromatic rings of the surface.

Vf copolymer	Time (h)	$M_n \times 10^4$	M_w/M_n	Content of Vf (mol%)
Poly(Vf-co-MMA)	24	1.3	1.23	9.3
Poly(Vf-co-St)	48	2.1	1.38	6.3

Note: Molar ratio in feed, Vf: vinyl monomer = 1:9; Temp., 70°C .

Table 1. Molecular weight, molecular weight distribution, and Vf content of Vf copolymers.

On the other hand, the grafting reaction successfully proceeded in the presence of AlCl_3 alone (Run 3). In the coexistence of AlCl_3 and Al powders, the grafting of poly(Vf-co-MMA) successfully proceeded and the percentage of grafting reached 54.1% after 24 h (Run 4). These results indicate that AlCl_3 receives cyclopentadienyl of ferrocene, and after the grafting of the copolymers onto GO, iron in ferrocene moiety exists in reduced form, because it is reported that Al powder prevents ferrocene from being oxidized to ferrocenium cation [32].

Figure 5 shows the relationship between reaction time and percentage of grafting during the ligand-exchange reaction of GO with poly(Vf-co-MMA) at 80°C. The percentage of poly(Vf-co-MMA) grafting increased with progress of the reaction and reached 54.2% after 24 h, but no longer increased after 24 h. This may be due to the fact that GO surface was blocked by previously grafted poly(Vf-co-MMA) chains.

Run	Catalyst		Grafting (%)
	AlCl_3 (10^{-4} mol)	Al powder (10^{-4} mol)	
1	–	–	0
2	–	1.8	0
3	7.0	–	21.0
4	7.0	1.8	54.1

Note: GO, 0.05 g; poly(Vf-co-MMA), 0.05 g; 1,4-dioxane, 10.0 mL, Temp., 80°C; 24 h.

Table 2. Effect of catalyst on the grafting of poly(Vf-co-MMA) onto GO by ligand-exchange reaction.

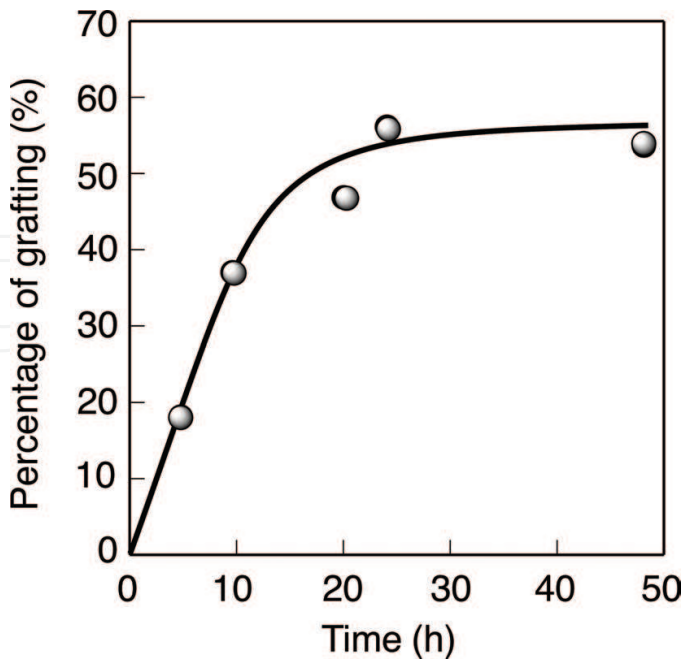


Figure 5. Grafting of poly(Vf-co-MMA) onto GO by ligand-exchange reaction of poly(Vf-co-MMA) with GO. GO, 0.05 g; poly(Vf-co-MMA), 0.05 g; AlCl_3 , 0.70 mmol; Al powder, 0.18 mmol; 1,4-dioxane, 10.0 mL; Temp., 80°C.

The grafting of poly(Vf-co-St) onto GO was also achieved by the ligand-exchange reaction of the corresponding copolymer with GO: the percentage of poly(Vf-co-St) grafting was determined to be 61.1%.

The mole number of grafted poly(Vf-co-MMA) and poly(Vf-co-St) on GO was estimated to be 4.2×10^{-5} and 3.0×10^{-5} mol/g, respectively. This may be due to the fact that the ferrocene content of poly(Vf-co-St) is smaller than that of poly(Vf-co-MMA).

3.4. Identification of poly(Vf-co-MMA)-grafted GO by GC-MS

The GC of thermally decomposed gas of untreated GO, GO-g-poly(Vf-co-MMA) and poly(Vf-co-MMA) is shown in **Figure 6**. It was observed that the generation of same thermally decomposed gas was generated at retention time 5.8 min. However, the small difference in thermal decomposition GC between poly(Vf-co-MMA) and GO-g-poly(Vf-co-MMA) was observed. The same results were reported in the case of poly(Vf-co-MMA)-grafted vapor grown carbon fiber and carbon black [17]. It can be presumed that that poly(Vf-co-MMA) was grafted by coordinate bonds with graphene structure of GO, as shown in **Scheme 2**.

The MS of decomposed gas of GO-g-poly(Vf-co-MMA) and poly(Vf-co-MMA) at retention time 5.8 min is shown in **Figure 7**. As shown in **Figure 7**, the MS of decomposed gas of GO-g-poly(Vf-co-MMA) was also in accord with that of poly(Vf-co-MMA): the structure of fragments at 56, 65, and 91 (m/z) estimated from MS database are also shown in **Figure 7**. These results clearly indicate that poly(Vf-co-MMA) was successfully grafted onto GO, and poly(Vf-co-MMA) was immobilized by coordinate bonds between the graphene structure of GO and the ferrocene moiety of poly(Vf-co-MMA) as mentioned above.

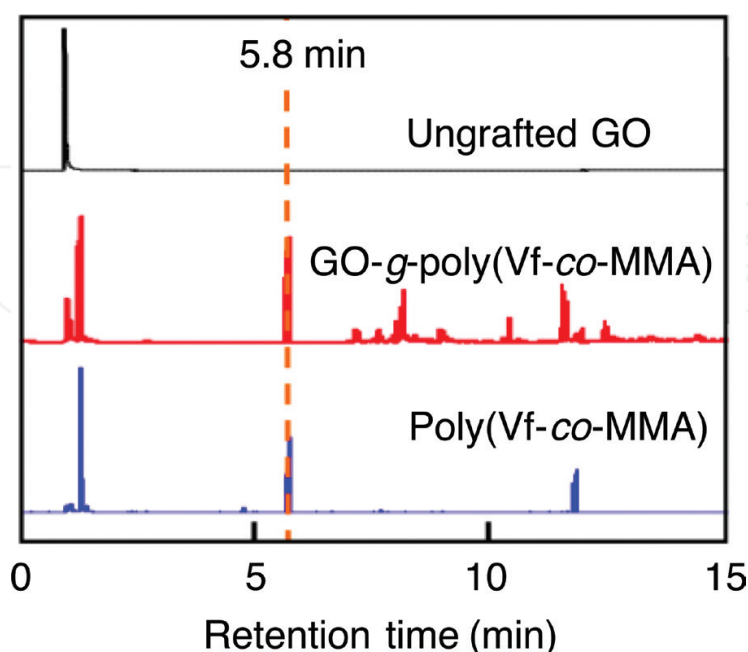


Figure 6. Thermal decomposition gas chromatograms of poly(Vf-co-MMA), GO-g-poly(Vf-co-MMA) and untreated GO.

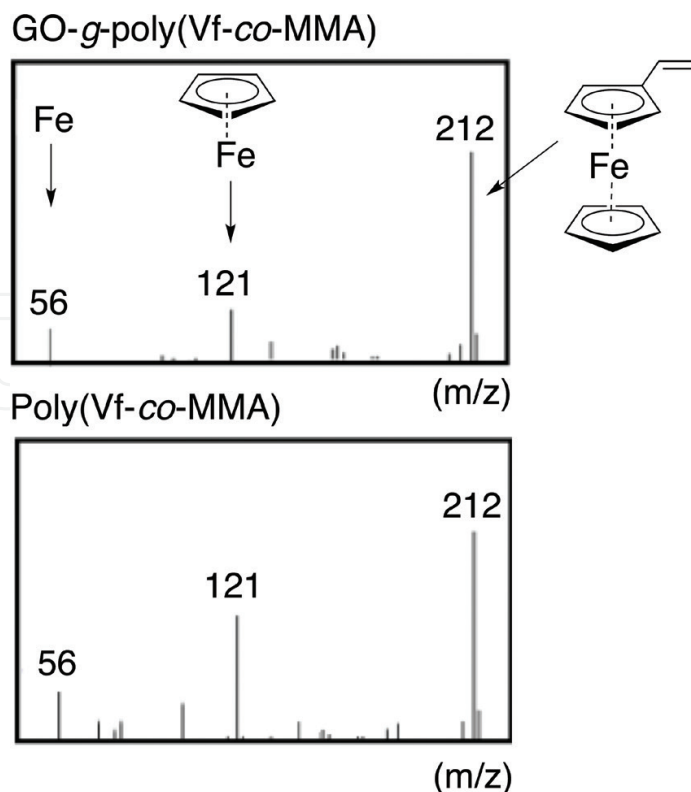


Figure 7. Mass spectra of decomposed gas of poly(Vf-co-MMA) and GO-g-poly(Vf-co-MMA) at retention time 5.8 min.

4. Cationic polymerization of vinyl monomers initiated by carboxyl groups on GO

4.1. Acidity of carboxyl groups on nanocarbons

We have pointed out that carboxyl (COOH) groups on nanocarbons, such as carbon black and vapor grown carbon fiber, have strong acidity, because of the effect of neighboring hydroxyl groups (*ortho*-effect) and have an ability to initiate the cationic polymerization of vinyl monomers to give the corresponding polymer-grafted nanocarbons.

For example, COOH groups on nanocarbons, such as carbon black and vapor grown carbon fiber, have strong acidity to initiate the cationic polymerization of vinyl monomers, such as vinyl ethers and *N*-vinylcarbazole (NVC) [25]. During the polymerization, the corresponding polymers were grafted onto these nanocarbon surfaces, based on the termination of growing polymer cation with surface carboxylate groups on GO as a counter anion.

4.2. COOH initiated cationic polymerization and grafting

The content of COOH and hydroxyl groups of GO used was determined to be 4.0 and 0.5 mmol/g, respectively. The content of COOH groups on GO used is much larger than

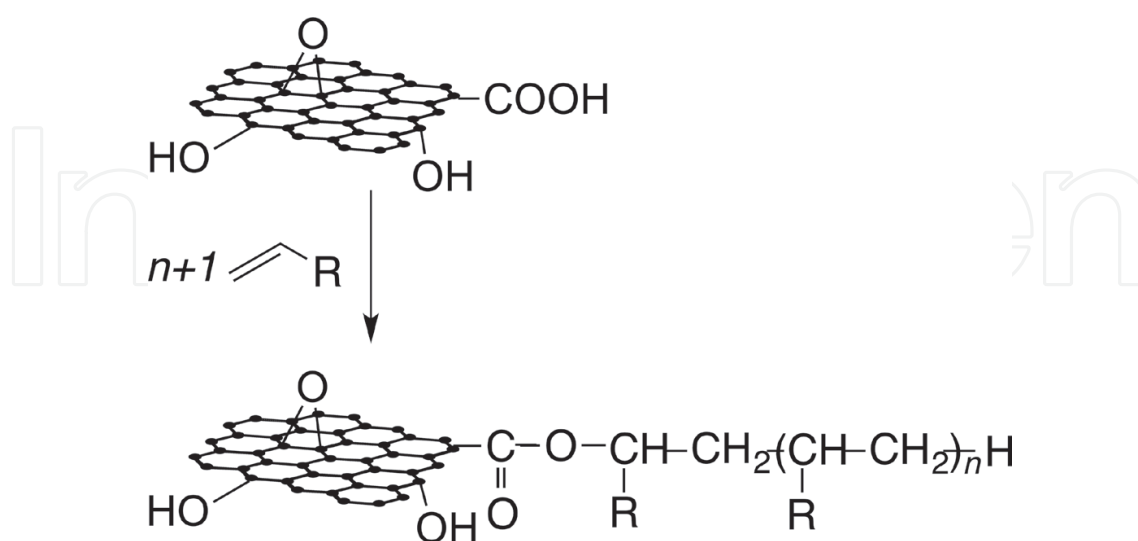
those of acidic carbon black; for example, the content of COOH groups on channel black FW 200 (Degussa AG.) is 0.61 mmol/g [28]. Therefore, it is expected that COOH groups on GO act as an effective initiator of the cationic polymerization of NVC, as shown in **Scheme 3**.

Figure 8 shows the relationship between conversion of NVC and reaction time during the polymerization of NVC in the presence of GO. As shown in **Figure 8**, the polymerization of NVC is successfully initiated even at 0°C and conversion of NVC increased with increasing reaction time and reached 95% after 12 h.

Figure 9 shows the FT-IR spectra of (A) polyNVC, (B) GO obtained from the cationic polymerization in the presence of GO, and (C) ungrafted GO. The FT-IR spectra of GO obtained from the polymerization in the presence of GO show characteristic absorptions of polyNVC. The result shows the grafting of polyNVC onto GO during the GO-initiated cationic polymerization of NVC.

Figure 10 shows the relationship between the percentage of polyNVC grafting onto GO and reaction time during the above-cationic polymerization. It was found that polyNVC was grafted onto GO, during the polymerization, and the percentage of grafting increased with increasing reaction time: the percentage of polyNVC grafting reached 14% after 12 h.

Figure 11 shows the relationship between conversion of isobutyl vinyl ether (IBVE) and reaction time during the GO-initiated cationic polymerization of IBVE. The conversion of IBVE increased with increasing reaction time and reached 78% after 1.5 h. The result indicates that GO also has an ability to initiate the cationic polymerization of IBVE.



Scheme 3. Cationic polymerization of vinyl monomers initiated by COOH groups on GO.

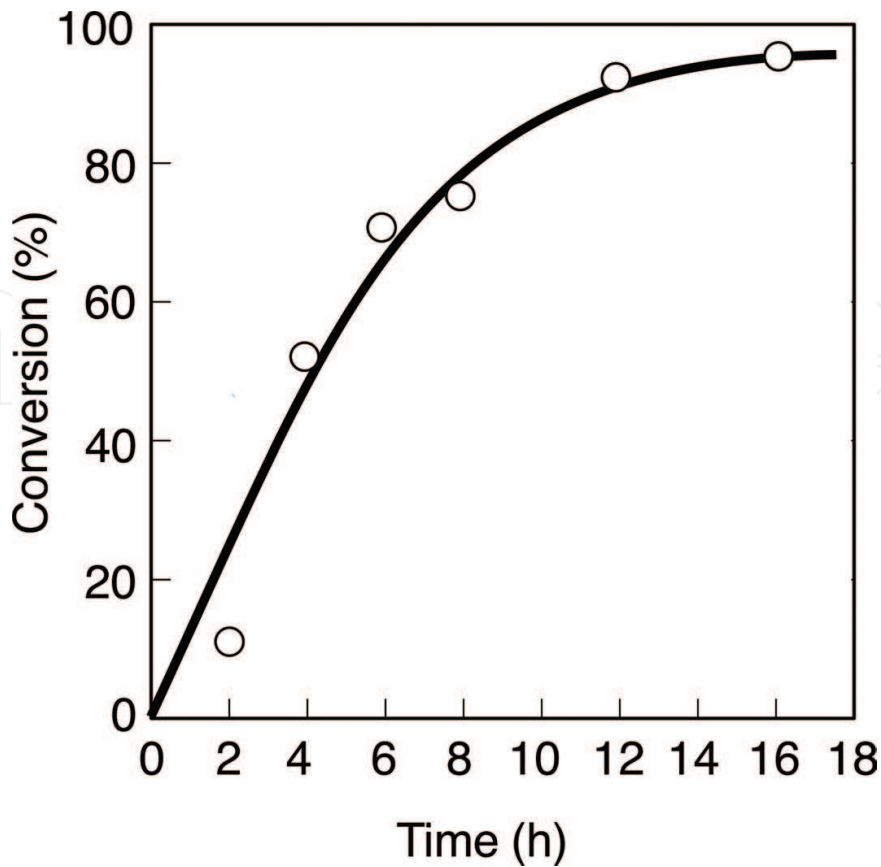


Figure 8. The relationship between conversion and polymerization time during the cationic polymerization of NVC initiated by COOH groups on GO. GO, 0.10 g; NVC, 1.0 g; toluene, 10 mL; Temp., 0°C.

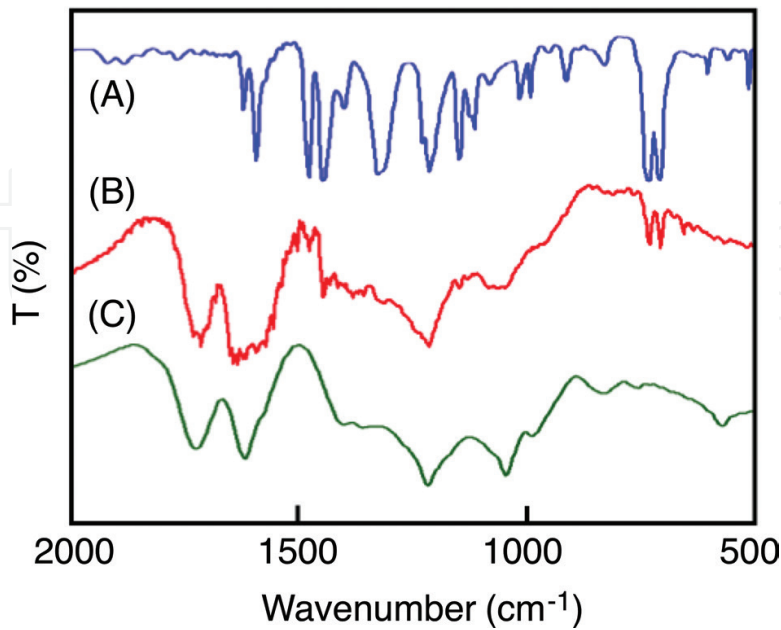


Figure 9. FT-IR spectra of (A) polyNVC obtained from the conventional cationic initiator, (B) GO obtained from the cationic polymerization of NVC in the presence of GO, and (C) ungrafted GO.

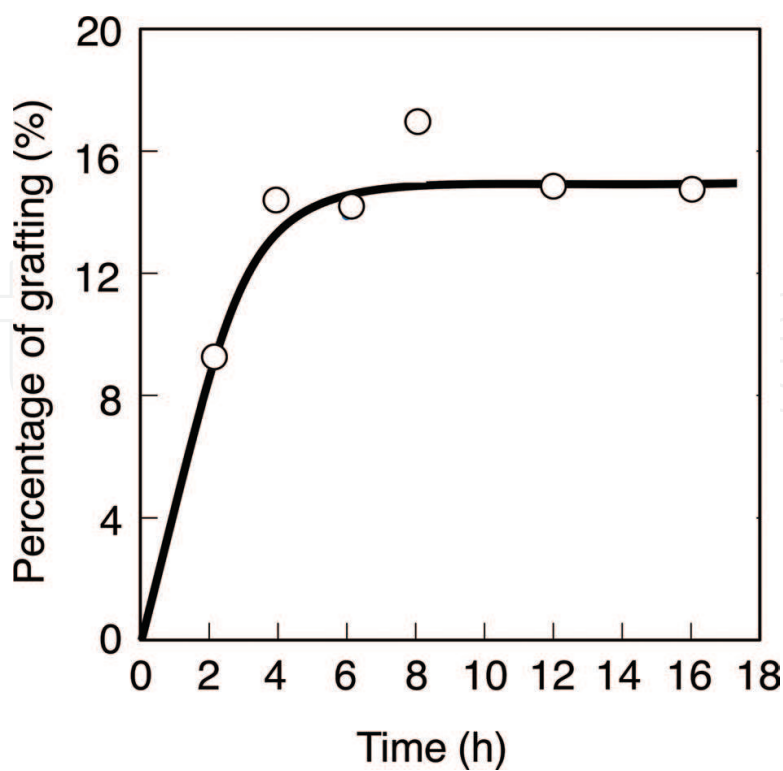


Figure 10. Relationship between percentage of polyNVC grafting onto GO and reaction time. Reaction conditions are shown in Figure 8.

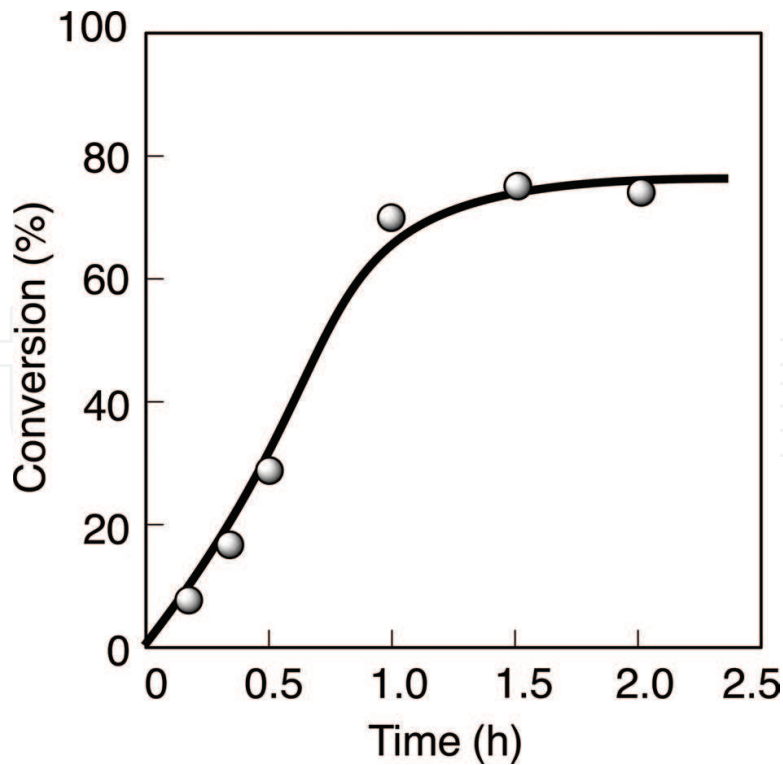


Figure 11. Cationic polymerization of IBVE initiated by COOH groups on GO. GO, 0.10 g; IBVE, 1.0 mL; toluene, 9.0 mL; Temp., 0°C.

4.3. Identification of polyIBVE grafting onto GO by GC-MS

The thermal decomposition GC of GO-*g*-polyIBVE, polyIBVE, and ungrafted GO is shown in **Figure 12(A)**. The thermal decomposition gas of GO-*g*-polyIBVE at retention time 1.2 min agreed with that of polyIBVE. On the other hand, the MS of thermally decomposed gas of polyIBVE and GO-*g*-polyIBVE at retention time 1.2 min is shown in **Figure 12(B)**. **Figure 12(B)** clearly shows that the MS of decomposed gas of GO-*g*-polyIBVE at retention time 1.2 min was in accord with that of polyIBVE: the parent peak at 74 (*m/z*) is considered to be isobutyl alcohol formed by the thermal decomposition of IBVE. The above results clearly indicate the grafting of polyIBVE onto GO during the GO-initiated cationic polymerization.

In addition, the GO-initiated polymerization of NVC and IBVE was completely inhibited by the addition of base, such as amines, indicating the initiation and propagation of the polymerization proceeded cationic polymerization mechanism.

4.4. Initiation and grafting mechanism

It is presumed that the cationic polymerization was initiated by proton addition of COOH groups on GO to vinyl monomer, as shown in **Scheme 4** (1) and then polymer chains propagated from carboxylate (COO⁻) groups on GO as a counter anion, as shown in **Scheme 4** (2). The grafting of the corresponding polymer onto GO is considered to be termination (neutralization) grafting reaction of propagating polymer cation with carboxylate anion (counter ion) on GO, as shown in **Scheme 4** [25, 28].

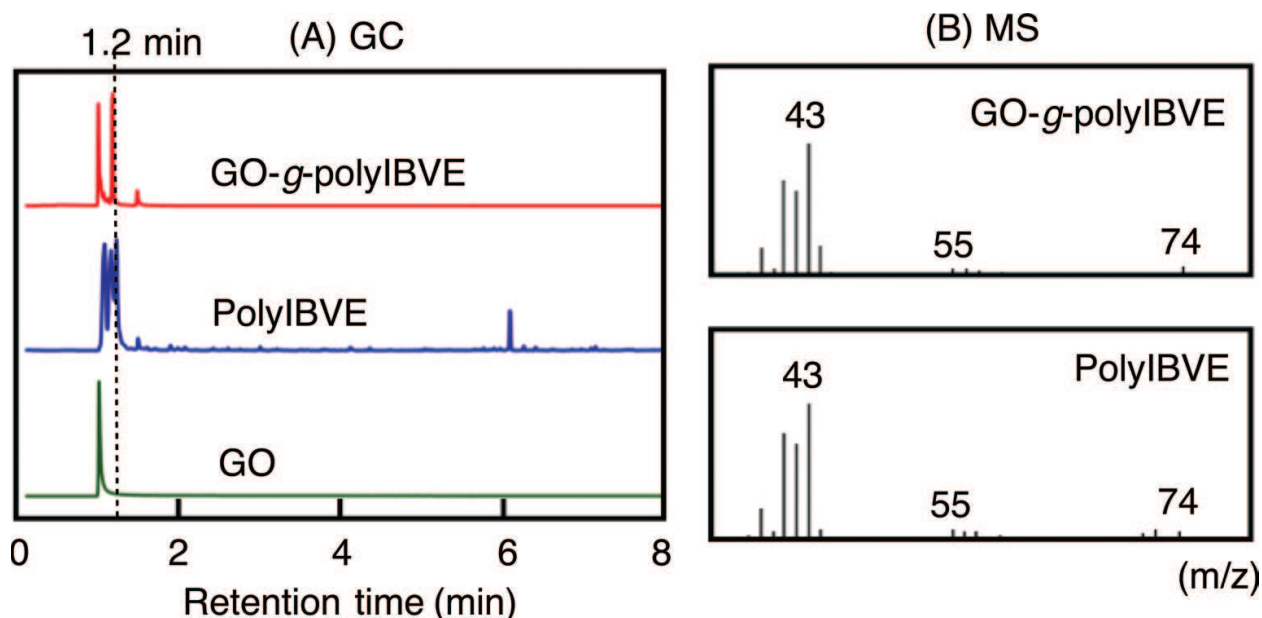
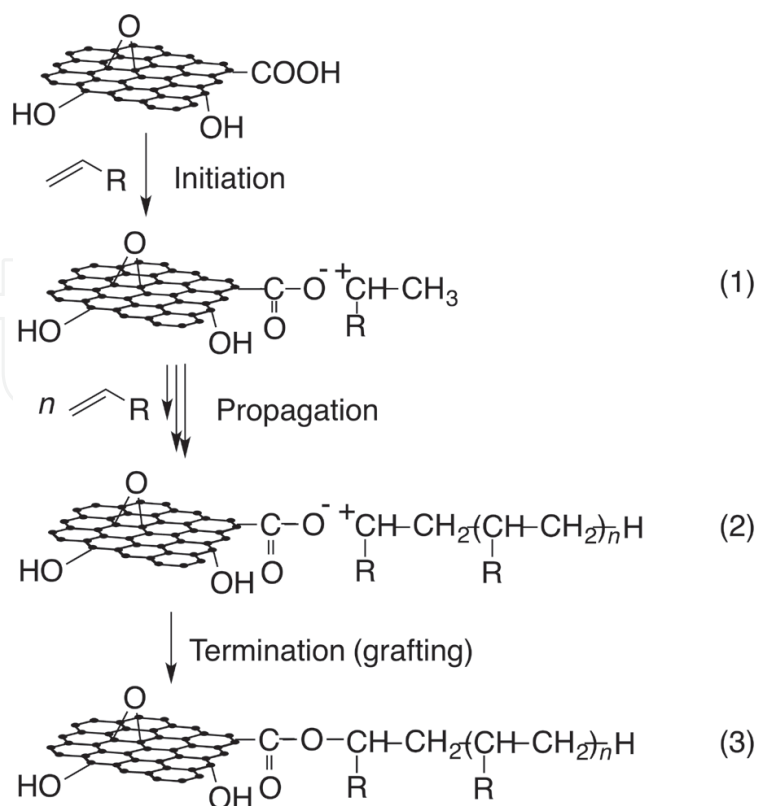


Figure 12. (A) Thermal decomposition GC of GO-*g*-polyIBVE, polyIBVE, and GO. (B) MS of thermal decomposition gas of GO-*g*-polyIBVE and polyIBVE at retention time 1.2 min.



- (1) Initiation by proton addition form COOH to monomer.
 (2) Propagation via GO-COO⁻ as counter anion.
 (3) Termination (neutralization) grafting of growing polymer cation with GO-COO⁻ as counter anion.

Scheme 4. Initiating and grafting mechanism of cationic polymerization of vinyl monomers initiated by COOH groups on GO.

5. Anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate groups on GO

5.1. Anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides

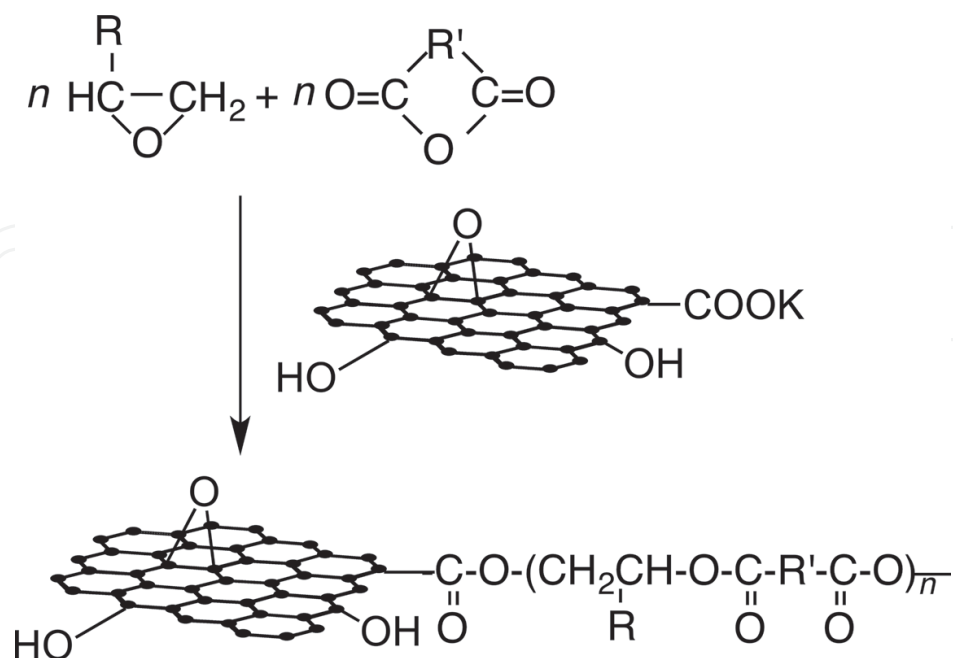
It is well known that alkali metal salts of aromatic carboxylic acid, such as potassium benzoate, have an ability to initiate the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides to give the corresponding polyester. On the other hand, we have reported, in the previous paper, that potassium carboxylate (COOK) groups introduced onto the surface of nanocarbons, such as carbon black and vapor grown carbon fiber, can initiate the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides and the corresponding polyester is readily grafted these nanocarbon surfaces [19, 20, 26, 28].

5.2. Anionic ring-opening alternating copolymerization initiated by COOK groups on GO

The anionic ring-opening alternating copolymerization of styrene oxide (SO) with phthalic anhydride (PAn) initiated by COOK groups on GO (GO-COOK) was examined (**Scheme 5**). GO-COOK can be readily prepared by the neutralization of COOH groups on GO with KOH. **Table 3** shows the results of the anionic ring-opening copolymerization of SO with PAn in the presence of GO-COOK under several conditions. In the polymerization, 18-crown-6 was added as an accelerator of the anionic copolymerization [19, 20, 26, 28].

As shown in **Table 3**, the ring-opening copolymerization of SO with PAn was hardly initiated in the presence of untreated GO (GO-COOH). In addition, no initiation of the anionic ring-opening polymerization of SO (or PAn) was observed even in the presence of GO-COOK. On the other hand, it was found that GO-COOK has an ability to initiate the anionic ring-opening alternating copolymerization of SO with PAn and the corresponding polyester, poly(SO-*alt*-PAn), was grafted onto GO.

The effect of polymerization time on the anionic ring-opening alternating copolymerization of SO with PAn [or maleic anhydride (MAN)] initiated by GO-COOK is shown in **Figure 13**. The copolymerization of SO with MAN was carried out in the presence of *N*-phenyl-naphthylamine (NPNA) in order to inhibit the radical cross-linking of formed unsaturated polyester, poly(SO-*alt*-MAN). It was found that the conversion increased with elapse of the polymerization time and the conversion of poly(SO-*alt*-PAn) and poly(SO-*alt*-MAN) exceeded 70 and 50% after 3 h at 120°C, respectively, suggesting the grafting of the corresponding polyester onto GO.



Scheme 5. Anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides initiated by COOK groups on GO.

GO	SO (mol)	PAn (mol)	Conversion (%)
GO-COOH	0.01	0.01	0
GO-COOK	0.01	–	0
GO-COOK	–	0.01	0
GO-COOH	0.01	–	72.0

Note: GO, 0.10 g; 18-crown-6, 0.02 g; Temp., 120°C; 8 h.

Table 3. Anionic ring-opening copolymerization of SO with PAn in the presence of GO-COOK and GO-COOH under several conditions.

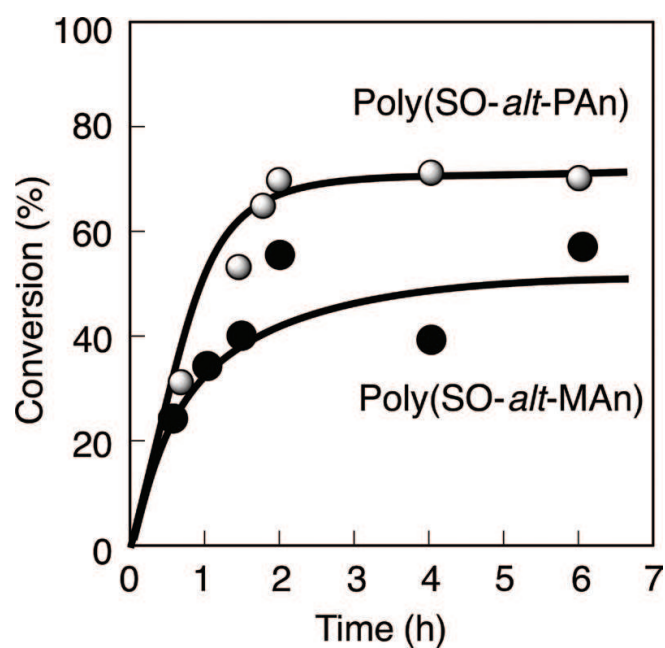


Figure 13. Effect of polymerization time on the anionic ring-opening alternating copolymerization of SO with PAn and MAn in the presence of GO-COOK. GO-COOK, 0.10 g; SO, 0.01 mol; cyclic acid anhydride, 0.01 mol; 18-crown-6, 0.02 mol; NPNA (in the case of MAn), 0.02 g, Temp., 120°C.

5.3. Identification of polyester-grafted GO by GC-MS

Figure 14(A) shows thermal decomposition GC of poly(SO-*alt*-PAn), which is obtained by using the conventional catalyst, GO-COOK, and GO-*g*-poly(SO-*alt*-PAn), obtained from the anionic ring-opening alternating copolymerization in the presence of GO-COOK. As shown in **Figure 14(A)**, the thermally decomposed gas of GO-*g*-poly(SO-*alt*-PAn) generated at retention time at 2.0 and 4.8 min was in accord with those of poly(SO-*alt*-PAn). In addition, the MS of thermally decomposed gas of poly(SO-*alt*-PAn) and GO-*g*-poly(SO-*alt*-PAn) at retention time 2.0 and 4.8 min, respectively, is shown in **Figure 14(B)** and **(C)**. It was found that the MS of thermally decomposed gas of poly(SO-*alt*-PAn)-grafted GO at retention time 2.0 min was in accord with that of poly(SO-*alt*-PAn), as shown in **Figure 14(B)**: the parent peak at 104 (m/z) was estimated to be the corresponding styrene generated by the thermal

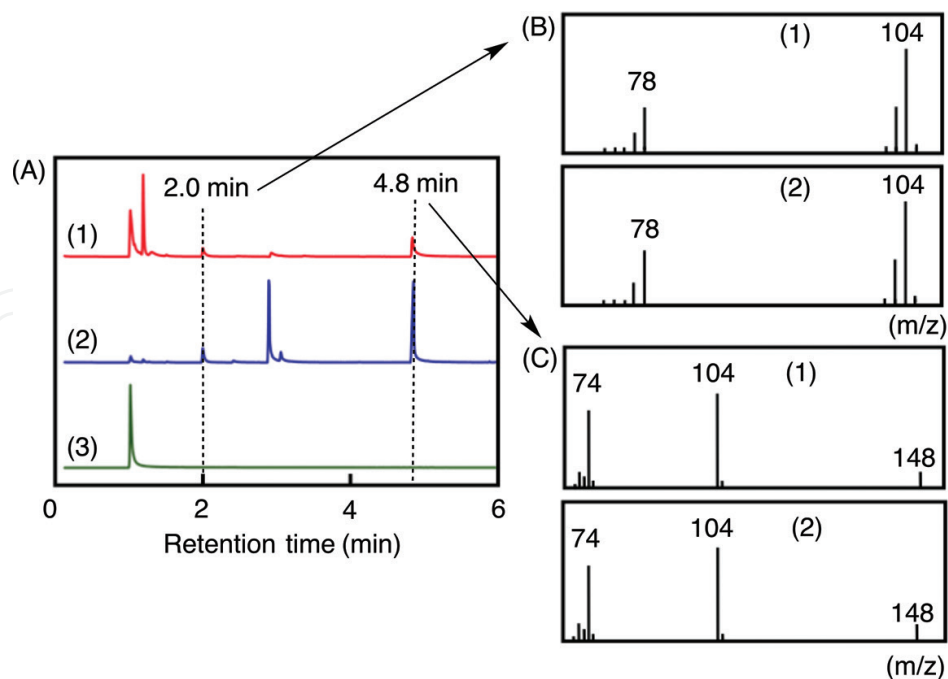


Figure 14. (A) Thermal decomposition gas chromatograms of (1) GO-g-poly(SO-*alt*-PAn), (2) poly(SO-*alt*-PAn), and (3) GO. (B) and (C) Mass spectra of thermal decomposition gas of GO-g-poly(SO-*alt*-PAn) and poly(SO-*alt*-PAn) at retention time 2.0 min and 4.8 min, respectively.

decomposition of poly(SO-*alt*-PAn). Furthermore, the MS of thermally decomposed gas of GO-g-poly(SO-*alt*-PAn) at retention time 4.8 min agreed with that of poly(SO-*alt*-PAn), as shown in **Figure 14(C)**; the parent peak at 148 (m/z) is estimated to be PAn generated by the thermal decomposition of poly(SO-*alt*-PAn). Based on the above results, it is concluded that poly(SO-*alt*-PAn) was successfully grafted onto GO during the anionic ring-opening copolymerization initiated by GO-COOK.

It was also confirmed by GC-MS that the grafting of poly(SO-*alt*-MAn) onto GO successfully achieved by the anionic ring-opening alternating copolymerization of SO with MAn initiated by GO-COOK.

6. Dispersibility of polymer-grafted GO in solvents

6.1. Dispersibility of GO obtained from radical trapping and ligand-exchange reaction

The untreated GO, GO-g-PEG, and GO-g-poly(Vf-co-MMA) were dispersed in good solvent of THF by the addition of the grafted polymer under irradiating ultrasonic wave and allowed to stand at room temperature. As a result, untreated GO precipitated within 15 min, but the dispersion of GO-g-PEG and GO-g-poly(Vf-co-MMA) in THF has excellent stability and precipitation of GO was scarcely observed even after 1 week at room temperature.

The stability of the GO dispersion in THF after the ultrasonic wave irradiation was also examined from the decrease of absorbance of GO dispersion at room temperature by use of UV-Vis spectrometer. The higher absorbance indicates no precipitation of GO, but lower absorbance indicates the precipitation of GO. As shown in **Figure 15**, untreated GO immediately precipitated, but the precipitation of GO-*g*-PEG and GO-*g*-poly(Vf-*co*-MMA) was scarcely observed, indicating the effect of grafting of polymers onto GO.

The results suggest that by the grafting of PEG and poly(Vf-*co*-MMA) onto GO surfaces, the aggregation of GO was successfully destroyed and grafted polymer chains onto the surface interfere with reaggregation of the GO in good solvents for grafted polymer, such as THF.

6.2. Dispersibility of GO obtained from surface-initiated cationic and anionic polymerization

Figure 16 shows the stability of dispersion of ungrafted GO, GO-*g*-polyNVC, GO-*g*-polyIBVE, and GO-*g*-poly(SO-*alt*-PAn) in THF at room temperature. Ungrafted GO precipitated completely within 3 h. On the contrary, polymer-grafted GOs gave stable dispersions in THF, a good solvent for grafted polymers.

Therefore, it is concluded that dispersibility of GO in THF was remarkably improved by grafting of polymers, such as polyNVC, polyIBVE, and polyesters.

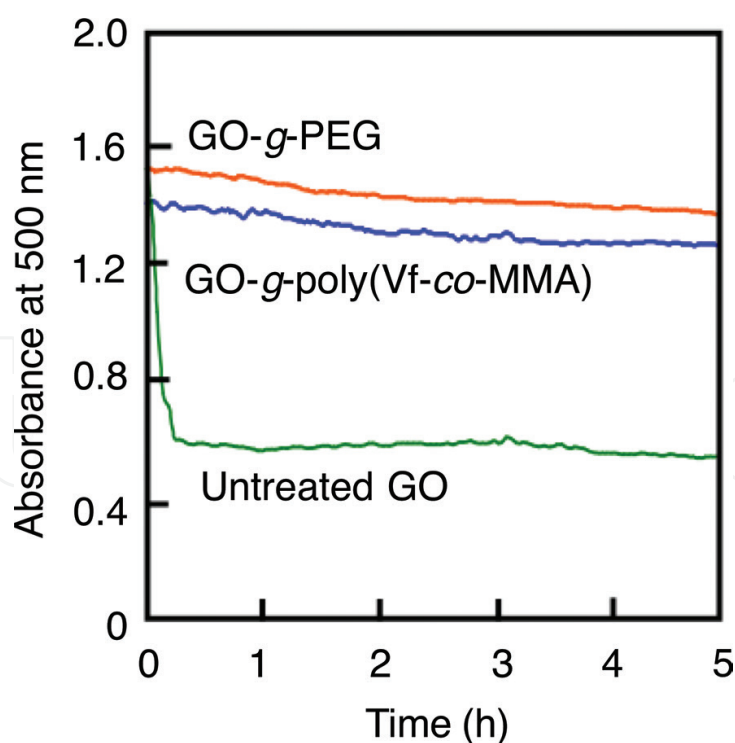


Figure 15. Dispersibility of GO-*g*-PEG and GO-*g*-poly(Vf-*co*-MMA) in THF at room temperature.

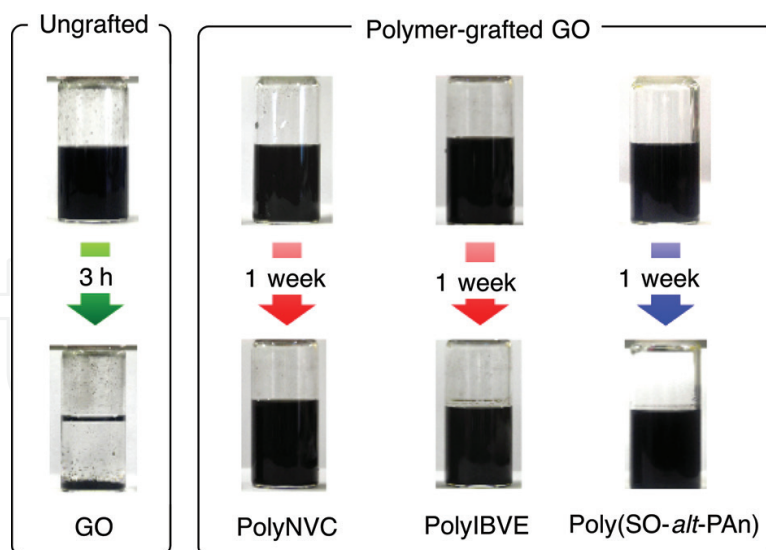


Figure 16. Dispersibility of ungrafted GO, GO-g-polyNVC, GO-g-polyIBVE, GO-g-poly(SO-*alt*-PAN) in THF at room temperature.

7. Easy preparation of reduced GO-based conducting polymer composite via organogel

Recently, we have reported that a highly electrically conducting graphene (reduced GO, rGO)-based polymer composite was successfully prepared via organogels using an organically dispersible electrically conductive polyaniline (polyANI) and a low molecular-weight organogelator consisting of cholesterol derivatives: organogelator used was complex salt of cholesterol hydrogen succinate with 1, 10-diaminodecane [33].

The plain gel was prepared by heat treatment of a mixture of toluene and the organogelator. PolyANI/rGO organogel was successfully obtained by the addition of polyANI and rGO to the plain gel and mixing them, as shown in **Figure 17**.

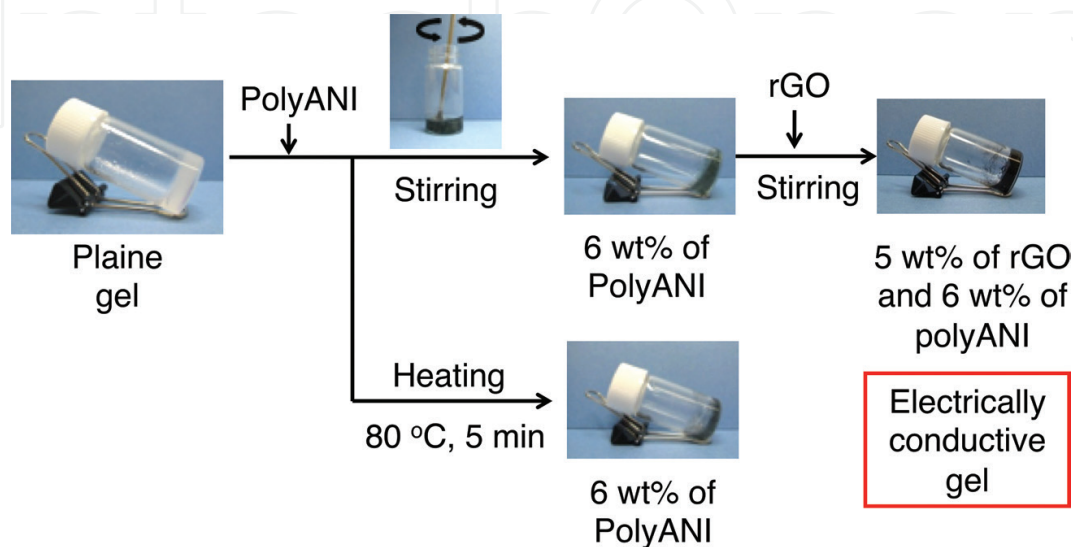


Figure 17. Easy preparation of polyANI/rGO organogel.

Similarly to the plain gel, polyANI/rGO organogels showed thixotropic behavior. It became apparent that these gels show a good recovery of viscoelasticity after the application of mechanical stress. Three-dimensional networks consisting of organogelators, polyANI aggregates, and rGO particles dispersed in the gel state were confirmed by the microscopic studies.

The value of electrical conductivity of the polyANI/rGO organogel is very low: it could be detected at 2.5×10^{-5} S/cm. The conductivity of dried polyANI/rGO composites synthesized via organogels was determined to be 3.2 S/cm. It is interesting to note that the contribution of the organogelator to form effective and complementary conducting pathways by polyANI and rGO.

A ballpoint pen was filled with the polyANI/rGO organogel and used to produce lines similar to the ones produced by commercially available ballpoint pen. It is interesting to note that the line showed electrical conductivity.

Acknowledgements

This work was supported by JSPS KAKENHI (grant number 24560836 and 24120008E).

Author details

Norio Tsubokawa^{1*}, Takeshi Yamauchi¹, Kazuhiro Fujiki² and Shingo Tamesue¹

*Address all correspondence to: ntsuboka@eng.niigata-u.ac.jp

1 Graduate School of Science and Technology, Niigata University, Niigata, Japan

2 Niigata Institute of Technology, Kashiwazaki, Niigata, Japan

References

- [1] Georgakilas V, editor. Functionalization of Graphene. Weinheim: Wiley-VCH; ISBN-13: 978-3527335510.
- [2] Hu K, Kulkarni D. D, Choi I, Tsukruk V. V: Graphene-polymer nanocomposites for structural and functional applications. Prog. Polym. Sci. 2014; **39**: 1934–72.
- [3] Song S, Zhai Y, Zhang Y: Bioinspired graphene oxide/polymer nanocomposite paper with high strength, toughness, and dielectric constant. ACS Appl. Mater. Interfaces. 2016; **8**: 31264–72.
- [4] Rajender N, Suresh K. I, Surface-initiated atom transfer radical polymerization (SI-ATRP) from graphene oxide: effect of functionalized graphene sheet (FGS) on the synthesis and material properties of PMMA nanocomposites. Macromol. Mater. Eng. 2016; **301**: 81–92.

- [5] Kumar A, Behera B, Thakre G. D, Ray S. S: Covalently grafted graphene oxide/poly(C-n-acrylate) nanocomposites by surface-initiated ATRP: an efficient antifriction, antiwear, and pour-point-depressant lubricating additive in oil media. *Ind. Eng. Chem. Res.* 2016; **55**: 8491–500.
- [6] Sun Y, Zhou J. H, Cheng Q, Lin D. S, Jiang Q, Dong A. J, Liang Z. C, Deng L. D: Fabrication of mPEGylated graphene oxide/poly(dimethylaminoethyl methacrylate) nanohybrids and their primary application for small interfering RNA delivery. *J. Appl. Polym. Sci.* 2016; **133**: 43303.
- [7] Huynh V. T, Duc N, Such C. H, Hawke B. S: Polymer coating of graphene oxide via reversible addition-fragmentation chain transfer mediated emulsion polymerization. *J. Polym. Sci. Part A: Polym. Chem.* 2016; **53**: 1423–21.
- [8] Gu R, Xu W. Z, Charpentier P. A: Synthesis of graphene-polystyrene nanocomposites via RAFT polymerization. *Polymer* 2016; **55**: 5322–31.
- [9] Travlou N. A, Kyzas, G. Z, Lazaridis N. K, Deliyanni A: Graphite oxide/chitosan composite for reactive dye removal. *Chem. Eng. J.* 2013; **217**: 256–65.
- [10] He L, Wang H, Xia G, Sun J, Song R: Chitosan/graphene oxide nanocomposite films with enhanced interfacial interaction and their electrochemical applications. 2014; **314**: 510–15.
- [11] Zuo P, Feng H, Xu Z, Zhang L, Zhang, Y, Xia W, Zhang W: Fabrication of biocompatible and mechanically reinforced graphene oxide-chitosan nanocomposite films. *Chem. Central J.* 2013; **7**: 39.
- [12] Yuan H, Meng L, Park S: A review: synthesis and applications of graphene/chitosan nanocomposites. *Carbon Lett.* 2016; **17**: 11–17.
- [13] Terzopoulou Z, Kyzas G. Z, Bikiaris D. N: Recent advances in nanocomposite materials of graphene derivatives with polysaccharides. *Materials* 2015; **8**: 625–83.
- [14] Terzopoulou Z, Kyzas G. Z, Bikiaris D. N: Recent advances in nanocomposite materials of graphene derivatives with polysaccharides. *Materials* 2015; **8**: 652–83.
- [15] Thakur V. K, Voicu S. I: Recent advances in cellulose and chitosan based membranes for water purification: a concise review. *Carbohydrate Polym.* 2016; **146**: 148–65.
- [16] Fang M, Wang K, Lu H, Yang Y, Nutt S: Single-layer graphene nanosheets with controlled grafting of polymer chains. *J. Mater. Chem.* 2010; **20**: 1982–92.
- [17] Ren L, Wang X, Guo S, Liu T: Functionalization of thermally reduced graphene by in situ atom transfer radical polymerization. *J. Nanopart. Res.* 2011; **13**: 6389–96.
- [18] Cui L, Liu J, Wang R, Liu Z, Yang W: A facile “grafting from” method to prepare molecular-level dispersed graphene-polymer composites. *J. Polym. Sci. Polym. Chem.* 2012; **50**: 4423–4432.
- [19] Tsubokawa N: Functionalization of carbon materials by surface grafting of polymers. *Bull. Chem. Soc. Japan.* 2002; **75**: 2115–36.

- [20] Tsubokawa N: Preparation and properties of polymer-grafted carbon nanotubes and nanofibers. *Polym. J.* 2005; **37**: 637–55.
- [21] Chen J, Wei G, Maekawa Y, Yoshida Y, Tsubokawa N: Grafting of poly(ethylene-block-ethylene oxide) onto a vapor grown carbon fiber surface by γ -ray radiation grafting. *Polymer*. 2003; **44**: 3201–7.
- [22] Wakai H, Shinno T, Yamauchi T, Tsubokawa N: Grafting of poly(ethylene oxide) onto C60 fullerene using macroazo initiators. *Polymer*. 2007; **48**: 1972–80.
- [23] Wei G, Saitoh S, Saitoh H, Fujiki K, Yamauchi T, Tsubokawa N: Grafting of vinyl polymers onto vapor grown carbon fiber surface by ligand-exchange reaction of ferrocene moieties of polymer with polycondensed aromatic rings of the wall-surface. *Polymer*. 2004; **45**: 8723–730.
- [24] Cha I, Shirai K, Fujiki K, Yamauchi T, Tsubokawa N: Surface grafting of polymers onto nanodiamond by ligand-exchange reaction of ferrocene moieties of polymers with polycondensed aromatic rings of the surface: *Diamond Related Mater.* 2011; **20**: 439–44.
- [25] Tsubokawa N, Maruyama H, Sone Y: Carbon fiber as an initiator of cationic polymerization of N-vinylcarbazole. *Polym. Bull.* 1986; **15**: 209–14.
- [26] Tsubokawa N, Hamada H, Sone Y: Grafting of polyesters from carbon fiber. Anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides initiated by COOK groups on the surface of carbon fiber. *Polym. Plast. Technol. Eng.* 1989; **28**: 201–14.
- [27] Cha I, Yagi Y, Kawahara T, Hashimoto K, Fujiki K, Tamesue S, Yamauchi T, Tsubokawa N: Grafting of polymers onto graphene oxide by trapping of polymer radicals and ligand-exchange reaction of polymers bearing ferrocene moieties. *Colloid Surf. A: Physicochem. Eng. Aspects*. 2014; **441**: 474–80.
- [28] Nagata K, Kawahara T, Hashimoto K, Fujiki K, Tamesue S, Yamauchi T, Tsubokawa N: Grafting of polymers onto graphene oxide by cationic and anionic polymerization initiated by the surface-initiating groups. *Composite Interfaces*. 2015; **22**: 25–37.
- [29] Ohkita K, Tsubokawa N, Saitoh E, Noda M: The free radical polymerization of vinyl monomers in the presence of carbon black. *Carbon*. 1975; **13**, 443–8.
- [30] Wako Pure Chemical Ind. Ltd. Japan: Macro azo-initiator [Internet]. 2016. Available from: <http://www.wako-chem.co.jp/kaseihin/macroazo/index.htm>.
- [31] Miyake M, Yasuda K, Kashiwara T, Teranishi T: Chemical modification of carbon hexagonal plane by ligand-exchange reaction. *Chem. Lett.* 1999; **28**: 1037–8.
- [32] Morrison Jr W. H, Ho E. Y, Hendrickson D. N: Reaction of ferrocene with polyaromatic molecules. π -Arene bis((π -cyclopentadienyl)iron) dications. *J. Am. Chem. Soc.* 1974; **96**: 3603–3608.
- [33] Kuwahara R. Y, Oi T, Hashimoto K, Tamesue S, Yamauchi T, Tsubokawa N: Easy preparation of graphene-based conducting polymer composite via organogel. *Colloid Polym. Sci.* 2015; **293**: 1635–45.

