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Facile Synthesis of Graft Copolymers Containing Rigid Poly(dialkyl fumarate) Branches by Macromonomer Method

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((Additional Supporting Information may be found in the online version of this article.))

ABSTRACT

Graft copolymers show microphase separated structure as seen in block copolymers and have lower intrinsic viscosity than block copolymers because of a branching structure. Therefore, considering molding processability, especially for polymers containing rigid segments, graft copolymers are useful architectures. In this work, graft copolymers containing rigid poly(diisopropyl fumarate) (PDiPF) branches were synthesized by full free radical polymerization process. First, synthesis of PDiPF macromonomers by addition-fragmentation chain transfer (AFCT) was investigated. 2,2-Dimethyl-4-methylene-pentanedioic acid dimethyl ester was found to be an efficient AFCT agent for diisopropyl fumarate (DiPF) polymerization because of the suppression of undesired primary radical termination, which significantly took place when common AFCT agent, methyl 2-(bromomethyl)acrylate, was used. Copolymerization of PDiPF macromonomer with ethyl acrylate accomplished the generation of the graft copolymer having flexible poly(ethyl acrylate) backbone and rigid PDiPF branches.

The graft copolymer showed a microphase separated structure, high transparency, and characteristic thermal properties to PDiPF and poly(ethyl acrylate).

INTRODUCTION

Graft copolymers are attractive architectures because they show similar properties to block copolymers such as a microphase separated structure and the intrinsic viscosity of a graft copolymer is lower than that of the corresponding block copolymer due to branching structures. There are three methods to synthesis graft copolymers, i.e., macromonomer (grafting through), grafting to, and grafting from methods, and each method has merits and demerits. We focused on a macromonomer method because graft copolymers with a relatively high branching density can be synthesized by conventional radical polymerization. Furthermore, graft copolymers having different arm polymers are synthesized by one-pot reactions using different macromonomers. Although living radical polymerization is one of the effective methods to synthesize macromonomers having a narrow molecular weight distribution and high end functionality, i.e., polymerizable group, macromonomers can also be conventionally synthesized by free radical polymerization using addition-fragmentation chain transfer (AFCT).¹⁻⁴ AFCT consists of two step elementary reactions, addition of a propagating radical to an AFCT agent and fast β -fragmentation of the resulting adduct radical.^{2,5,6} Some of α -(substituted methyl)vinyl compounds acts as AFCT agents in styrene and (meth)acrylates polymerizations and polymers having 2-substituted-2-propenyl group at the ω -end, i.e., macromonomers, are generated.⁷ Vinyl monomer-based graft copolymer syntheses using the macromonomers prepared by AFCT were also reported.^{3,8-11}

Dialkyl fumarates are 1,2-disubstituted vinyl monomers and undergo radical high polymerization to generate poly(substituted methylene)s, which do not contain a rotatable

methylene group in the main chain and show rigid nature as a polymer obtained from vinyl monomers. Poly(dialkyl fumarate)s possess high transparency,¹² good gas permeability,¹³ and high thermal stability,¹⁴ and are useful industrial polymeric materials. To modify poly(dialkyl fumarate)s with maintaining their poly(substituted methylene) structure, graft and block copolymers containing a poly(dialkyl fumarate) chain are required. Block copolymers consisting of rigid poly(diisopropyl fumarate) (PDiPF) and flexible poly(meth)acrylate segments were successfully synthesized by using living radical polymerization techniques.¹⁵ However, limitations regarding to the order of polymerization of fumarates and (meth)acrylates were pointed out in the report, and thus the synthesis of block copolymers containing multiple poly(dialkyl fumarate) segments is expected to be difficult. Although the details are not clear, exceptional radical polymerization behavior of fumarate seems to be one of the reasons for the difficulty in the living radical polymerization. That is, in the radical polymerization of dialkyl fumarate such as diisopropyl fumarate (DiPF), both propagating and bimolecular termination rate constants are exceptionally small compared with conventional vinyl monomers due to the steric hindrance of DiPF and a PDiPF propagating radical.¹⁶ Since not only propagation but also termination are suppressed, relatively high-molecular-weight PDiPF is generated in a normal polymerization rate. In the living radical polymerization, the chance of propagation is limited because most of propagating radicals are inactivated as dormant species, and slow propagation of fumarate seems to cause problem. In addition to the aforementioned general merit of graft copolymers over block copolymers, in the case of fumarates, graft copolymers are more suitable platform to introduce multiple poly(dialkyl fumarate) chains than block copolymers. In this study, efficient synthesis poly(diisopropyl fumarate) macromonomers (PDiPF MMs) by AFCT were investigated and it was found that 2,2-dimethyl-4-methylene-pentanedioic acid dimethyl

ester (unsaturated dimer of MMA; MMAD) showed better AFCT ability than methyl 2-(bromomethyl)acrylate (MBMA), which is one of the most efficient AFCT agent for styrene, methacrylates, and acrylates. Graft copolymers consist of flexible poly(ethyl acrylate) as a backbone polymer and PDiPF as branches were also successfully synthesized by full free radical process using PDiPF MM. Thermal, optical, and morphological properties of the resulting graft copolymer were also investigated.

EXPERIMENTAL

Materials

MBMA¹⁷ and MMAD¹⁸ were synthesized based on the literatures. DiPF and ethyl acrylate (EA) were distilled under reduced pressure at 120 °C/< 1 mmHg and at 80 °C/60 mmHg, respectively. 2,2'-Azobis(isobutyronitrile) (AIBN) and 2,2'-azobis(cyclohexane-1-carbonitrile) (ACN) were recrystallized from methanol and MBMA was recrystallized from *n*-hexane, and they were dried under vacuum for 12 h. 2,2'-Azobis(2,2,4-trimethylpentane) (ATMP) and 2,2'-azobis(2-methylpropane) (AMP) (test samples from Wako Pure Chemical Industries, Ltd. (Osaka, Japan)) were distilled under reduced pressure (160 °C/5 mmHg) and used as received, respectively.

Polymerization

Radical bulk polymerization of DiPF in the presence of and the absence of an AFCT agent was carried out under vacuum in a sealed glass tube. After polymerization, the polymerization mixture was quenched by cooling in ice-bath and the mixture was submitted to GPC and ¹H NMR analysis to determine conversion of DiPF and AFCT agent. The resulting macromonomer,

PDiPF MM, was isolated by reprecipitation in the mixed precipitant, methanol/water = 4/1 (vol./vol.), for two times.

Copolymerization of PDiPF with EA was similarly carried out in toluene at 65 °C for 48 h. After quenching polymerization, the reaction mixture was submitted to GPC and ^1H NMR analysis. The resulting graft copolymer, PEA-*g*-PDiPF, was isolated by reprecipitation in the mixed precipitant, acetone/*n*-hexane = 1/9 (vol./vol.), to remove unreacted PDiPF MM.

Measurements

Bruker Avance 300 was used for ^1H NMR measurement, and deuterated chloroform was used as a solvent. For GPC measurement, Tosoh CCPD RE-8020 was used with THF as an eluent. The number average molecular weight (M_n) and the weight average molecular weight (M_w) were determined from the calibration curve of standard polystyrenes. For thermogravimetric/differential thermal analysis (TG/DTA), TG/DTA 6200 manufactured by Seiko Instruments Inc. was used at a temperature rising rate of 10 °C/min under nitrogen stream (200 mL/min). For the differential scanning calorimetry (DSC), DSC 6200 manufactured by Seiko Instruments Inc. was used at a heating rate of 25 °C/min under a nitrogen stream (50 mL/min). Spin coat films were prepared by using a spin coater, MS-B100 (Mikasa). Shimadzu UV-2400 was used for transmittance measurement. Atomic force microscope (AFM) images were measured using a Nanoscope IIIa SPM system manufactured by Digital Instruments and an MMAFM multimode SPM unit. As a cantilever, PMCL-AC240TS-C2 (OLYMPUS) or PMCL-AC240TS-C3 (OLYMPUS) was used.

RESULTS AND DISCUSSION

Synthesis of PDiPF Macromonomer

Radical polymerization of DiPF was carried out at 80 to 148 °C in the presence of MBMA, which is one of the most efficient AFCT agent for vinyl monomers such as styrene, acrylate, methacrylate, and their derivatives.^{2,19} The results of the polymerization are summarized in Table 1 together with the results in the absence of MBMA as a comparison. To avoid the consumption of the resulting PDiPF by further copolymerization with DiPF, which will result in PDiPF macromonomer having branching structures, the polymerization in the presence of MBMA was quenched at low DiPF conversions. The effect of the further copolymerization is expected to increase with increasing DiPF conversion because the relative concentration of the 2-substituted-2-propenyl group in the macromonomer to DiPF increases. The ¹H NMR spectrum of the isolated PDiPF MM obtained by run 4 in Table 1 is shown in Figure 1 as a representative data. In Figure 1, the peaks assignable to the 2-methoxycarbonyl-2-propenyl group generated by AFCT (*d*, *e*, *f*, and *g*) was clearly observed in addition to the peaks due to a DiPF repeating unit (*a*, *b*, and *c*). The number average molecular weight ($M_{n,NMR}$) was calculated by the relative intensities of the peaks *b*, *f*, and *g*, assuming that all polymer chains have the 2-substituted-2-propenyl group. The value of $M_{n,GPC}/M_{n,NMR}$ can be used as an index of the ratio of polymer having 2-substituted-2-propenyl by AFCT. PDiPF is a rigid poly(substituted methylene) and one may concern that the $M_{n,GPC}$ values contain a large error due to the difference in the Mark-Houwink-Sakurada parameters of PDiPF and polystyrene used for the GPC calibration. It has been reported that in the living radical polymerization of DiPF, the difference between the $M_{n,GPC}$ value determined by polystyrene standards calibration and the $M_{n,NMR}$ value determined by the characteristic peaks due to the ω -end group and DiPF repeating unit was less than 10%, and also the $M_{n,GPC}$ values agreed with the theoretical values.¹⁵ Based on the fact, it is reasonable expected that the $M_{n,GPC}$ values determined in this study do not contain a large error and the

$M_{n, \text{GPC}}/M_{n, \text{NMR}}$ values can be used to discuss a trend in the series of experiments. In Table 1, at all temperatures, the value of $M_{n, \text{GPC}}/M_{n, \text{NMR}}$ was low, i.e., 26% to 35%. However, in all cases, $M_{n, \text{GPC}}$ value significantly decreased in the presence of MBMA compared to that in the absence of MBMA, and it is suggested that chain transfer to MBMA took place.

The low $M_{n, \text{GPC}}/M_{n, \text{NMR}}$ values, i.e., an insufficient introduction of the 2-methoxycarbonyl-2-propenyl group at the ω -end, can be rationalized by the occurrence of significant primary radical termination of a PDiPF propagating radical with bromine atom, which is generated by β -fragmentation of the adduct radical from a PDiPF propagating radical and MBMA (Scheme 1). Frequent primary radical termination decreases the contribution of AFCT to the chain end forming events and generates a dead polymer without the 2-substituted-2-propenyl group at the ω -end, i.e., a decrease in the $M_{n, \text{GPC}}/M_{n, \text{NMR}}$ value. In DiPF polymerization, bimolecular termination of the propagating radicals is markedly suppressed by the steric hindrance around the radical center,¹⁶ and primary radical termination of the PDiPF propagating radical with less hindered bromine atom is expected to proceed much faster than the bimolecular termination. As a result, polymers having 2-methoxycarbonyl-2-propenyl group at the ω -end decreased.

It is reported that radical polymerization behavior of fumarates is strongly influenced by the type of primary radicals, i.e., the structure of initiators.^{20,21} For example, AIBN generating 2-cyano-2-propyl radical resulted in much slower polymerization rate and slightly lower molecular weight of a polymer than the case of MAIB generating 2-(methoxycarbonyl)-2-propyl radical. The different polymerization behavior was rationalized by a lower initiation reactivity and a larger contribution of the primary radical termination of a 2-cyano-2-propyl radical from AIBN. Based on this fact, we conceived that an AFCT agent expelling the same radical as the primary radical from MAIB, i.e., 2-(methoxycarbonyl)-2-propyl radical, will reduce the contribution of

primary radical termination and smoothly reinitiate polymerization of DiPF. We selected MMAD as an AFCT agent satisfying this requirement.^{22,23} MMAD is a copolymerizable AFCT agent and it has been revealed that it is necessary to be used at a high temperature to suppress the copolymerization and promote AFCT.²² Polymerization of DiPF in the presence of MMAD as an AFCT agent was carried out at high temperature, i.e., 128 and 148 °C, and the results are summarized in Table 1 (run 7 and 10). The representative ¹H NMR spectra is shown in Figure 2. In addition to the peaks assignable to DiPF repeating unit (*a*, *b*, and *c*), the peaks due to 2-methoxycarbonyl-2-propenyl group at the ω-end (*d*, *e*, *f*, and *g*) and 2-(methoxycarbonyl)-2-propyl group at the α-end (*h* and *i*) were observed. The $M_{n, \text{GPC}}/M_{n, \text{NMR}}$ value was calculated by using relative peak intensities of peaks *b*, *f*, and *g*. At 128 °C, the $M_{n, \text{GPC}}/M_{n, \text{NMR}}$ value was 54% and is twice higher than that obtained in the presence of MBMA (= 26%). At 148 °C, the $M_{n, \text{GPC}}/M_{n, \text{NMR}}$ value was further increased to 72%, and PDiPF MM having relatively high ω-end functionality was successfully synthesized by using MMAD at the high temperature.

There is a possibility that the resulting PDiPF MM consumed by copolymerization

Graft Copolymerization of PDiPF Macromonomer

Graft copolymerization of PDiPF MM with an acrylate giving a low T_g polymer, i.e., EA, was carried out using the isolated PDiPF MM prepared in the presence of MBMA or MMAD (Table 2). Copolymerization was performed at 65 °C for 48 h, and EA reached almost full conversion in each case. The GPC elution curves of the reaction mixture are shown in Figure 3 together with those of PDiPF MM. When PDiPF MM prepared by MBMA was used, a significant amount of low molecular weight fraction, the peak top of which is the same as that of PDiPF MM, remained after copolymerization (Figure 3(a)). The $M_{n, \text{GPC}}/M_{n, \text{NMR}}$ value of PDiPF MM

used in this polymerization is low ($M_{n, \text{GPC}}/M_{n, \text{NMR}} \times 100 = 27\%$), i.e., low ω -end functionality, and the PDiPF without a polymerizable ω -end group remained as a low molecular weight fraction. In the case of PDiPF MM prepared by MMAD ($M_{n, \text{GPC}}/M_{n, \text{NMR}} \times 100 = 57\%$), although there are still unreacted low molecular weight fraction, the ratio of which to the newly generated high molecular weight fraction is smaller than the case of MBMA (Figure 3(b)). These results show that PDiPF MM having higher ω -end functionality results in more efficient graft copolymer synthesis. In both cases, the molecular weight distribution of the remaining PDiPF MM after copolymerization showed almost the same at that of PDiPF MM used for the copolymerization. Therefore, it is expected that the consumed PDiPF MM, which is introduced to the graft copolymer as a branch, has also the same molecular weight to the original PDiPF MM. Careful selection of precipitation solvents accomplished an effective removal of the remaining PDiPF MM and an isolation of the resulting graft copolymer, PEA-g-PDiPF (Figure 3(b)). The ^1H NMR spectra of the isolated PEA-g-PDiPF (PEA-g-PDiPF(MMAD-1)) is shown in Figure 4. Characteristic peaks assignable to EA repeating unit and DiPF repeating unit were observed. Furthermore, the peak corresponding the methoxy carbonyl group adjacent to the vinyl group, which was observed at around 3.7 ppm (the peak *e*) in Figure 2, was disappeared in Figure 4. This shows that the 2-methoxycarbonyl-2-propenyl group in PDiPF MM was consumed by copolymerization with EA and PDiPF was incorporated as branches in the resulting graft copolymer. The copolymer composition of PEA-g-PDiPF(MMAD-1) was determined to be $d[\text{EA}]/d[\text{DiPF}] = 69/31$ based on the characteristic ^1H NMR peaks for each monomer unit. From the $M_{n, \text{GPC}}$ value and the copolymer composition of PEA-g-PDiPF(MMAD-1), and the $M_{n, \text{GPC}}$ value of the PDiPF MM, the number average degree of polymerization of PEA backbone and the average number of PDiPF branches per a graft

copolymer molecule was calculated to be 263 and 4, respectively. It was reported that vinyl monomer-based macromonomers having a 2-substituted-2-propenyl group, which is one of α -(substituted methyl)vinyl compounds, play two roles in the radical polymerization of vinyl monomers, that is the macromonomer acts as a comonomer and/or AFCT agent.¹⁰ The contribution of the macromonomers as a comonomer, an AFCT agent, or both, changes depending on the vinyl monomer to be copolymerized and the structure around the 2-substituted-2-propenyl group in the macromonomer. In this study, 4 PDiPF branches were introduced into the graft copolymer in average and it was revealed that PDiPF MM has a copolymerizability with EA.

Thermal Properties

The DSC curve of PEA-g-PDiPF(MMAD-2), which was synthesized and isolated in the same ways as PEA-g-PDiPF(MMAD-1) (Table 2), is shown in Figure 5. Two endothermic shifts were observed at -13 °C and 54 °C in the first heating step, which was measured after quenching the sample to -150 °C. The T_g value of PEA ($M_n = 51,000$) measured under the same conditions as Figure 5 was -20 °C and the endothermic shift at -13 °C in Figure 5 is due to the glass transition of PEA in the backbone of PEA-g-PDiPF. The slight increase in T_g from -20 °C for the linear PEA to -13 °C for the graft copolymer may be attributed to the suppression of the micro-brownian motion by the presence of rigid PDiPF as the branches. The endothermic shift at 54 °C is assignable to β -transition of PDiPF, i.e., the motion of ester group in the side-chain of PDiPF. PDiPF is reported to show α -relaxation, i.e., T_g , at ca. 260 °C, where decomposition of PDiPF also proceeds.¹⁴ Several literatures reported the temperatures of β -transition determined by DSC, and the values range from 62 to 74 °C.^{12,24} The currently observed β -relaxation (54 °C) is slightly lower than those reported in the literatures. The M_n of the PDiPF branch in PEA-g-

PDiPF is 4,900 and is much smaller than those used in the literatures ($M_n = 37,000$ to $80,000$). The lower M_n of the PDiPF branch may somehow decrease the β -relaxation. In the cooling step after the first heating step, i.e., the first cooling step, the two endothermic shifts were observed at corresponding temperatures to those shifts observed in the first heating step and demonstrated that the two endothermic shifts observed in the first heating step are due to a reversible relaxation. In the second heating step, endothermic shift due to the β -transition of PDiPF was unclear, probably due to the effect of thermal history.

The TG and DTG curves of PEA-g-PDiPF(MMAD-2) are shown in Figure 6 together with those of PDiPF and PEA. PEA-g-PDiPF resulted in a two-step thermal decomposition. The first decomposition step corresponds to the side-chain decomposition of the PDiPF branch, which contains the secondary ester groups being less thermally stable than the primary ester group of PEA. The second decomposition step of EA-g-PDiPF is due to the side-chain decomposition of the PEA backbone and main-chain decomposition of PDiPF and PEA.

Morphology

The spin coated film of PEA-g-PDiPF(MMAD-1) was prepared on glass plate using a 100 μ L of chloroform solution containing 2.5 wt% of the polymer (at 250 rpm for 10 sec and subsequently at 2500 rpm for 40 sec). The AFM height and phase images of the spin coated film is shown in Figure 7(a) and (b), respectively. The film surface evaluated by AFM height image was very smooth (Figure 7(a)). In the phase image, although the structure is not very clear, microphase separated structure in the order of 10^1 nm was observed (Figure 7(b)). The polymer blend of PDiPF and PEA showed much larger phase separated structure (in the order of 10^3 nm) (see Figure S1 in the Supporting Information), and the microphase separation in the order of 10^1 nm

in Figure 7(b) can be attributed to the graft copolymer. The relatively low M_n of the PDiPF branch may account for the unclear microphase separates structure.

Optical and Mechanical Properties

The cast film of PEA-g-PDiPF(MMAD-1) was prepared from 1,2-dichloroethan solution containing 20 wt% of the polymer. The solution was casted on quartz and dried at r.t. for 1 day and under reduced pressure for 2 days to obtain a visually transparent film. The Transmittance of the PEA-g-PDiPF(MMAD-1) cast film (film thickness = 110 μm) is shown in Figure 8. The film was highly transparent from UV to visual reasons and transmittance values were 97% at 300 nm and almost 100% at 400 nm. The cast film of PEA-g-PDiPF(MMAD-1) and PDiPF ($M_n = 55,200$, $M_w/M_n = 1.31$) were similarly prepared on a Teflon plate. As shown in Figure 9(a) and (b), the PEA-g-PDiPF(MMAD-1) cast film was readily removed from a Teflon plate and was sufficiently flexible so as not to break even when bent about 90°. In stark contrast, the PDiPF cast film was brittle and was broken when it was peeled from a Teflon plate.

CONCLUSIONS

Synthesis of PDiPF MM was investigated by free radical polymerization in the presence of AFCT agents. Because of the unique polymerization behavior of DiPF, MBMA, which is efficient AFCT agent for styrene and (meth)acrylates, resulted in significant primary radical termination and thus poor introduction of 2-methoxycarbonyl-2-propenyl end group, i.e., low functionality of the macromonomer (26-35%). MMAD was selected as the AFCT agent, which expels 2-(methoxycarbonyl)-2-propyl radical and was expected to reduce the contribution of the primary radical termination. MMAD achieved much higher end functionality (72%) than the case of MBMA under the comparable polymerization conditions. PDiPF MM synthesized by

using MMAD was copolymerized with EA to generate the graft copolymer consist of flexible backbone and rigid branches. The resulting graft copolymer, PEA-g-PDiPF, showed microphase separated structure in the order of 10^1 nm and was highly transparent from UV to visible regions. Furthermore, PEA-g-PDiPF was more flexible than PDiPF due to the PEA backbone. The results show that the graft copolymers consist of polyacrylate backbone and PDiPF branches can be synthesized by only free radical polymerization process and flexibility can be provided with maintaining PDiPF properties arising from poly(substituted methylene) structure by using graft copolymer architecture.

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REFERENCES AND NOTES

1. G. F. Meijs, T. C. Morton, E. Rizzardo, S. H. Thang. *Macromolecules* **1991**, *24*, 3689-3695.
2. B. Yamada, P. B. Zetterlund, E. Sato. *Prog. Polym. Sci.* **2006**, *31*, 835-877.
3. C. P. R. Nair, P. Chaumont, C. Chmrot. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2511-2524.
4. E. Sato, P. B. Zetterlund, B. Yamada. *J. Polym. Sci.: Part A: Polym. Chem.* **2004**, *42*, 6021-6030.
5. G. F. Meijs, E. Rizzardo, S. H. Thang. *Polym. Bull.* **1990**, *24*, 501-505.
6. D. Colombani, P. Chaumont. *Prog. Polym. Sci.* **1996**, *21*, 439-503.
7. B. Yamada, S. Kobatake. *Prog. Polym. Sci.* **1994**, *19*, 1089-1131.

8. C. P. R. Nair, P. Chaumont, D. Charmot. *Polymer* **1999**, *40*, 211-2119.
9. S. A. F. Bon, S. R. Morsley, C. Waterson, D. M. Haddleton. *Macromolecules* **2000**, *33*, 5819-5824.
10. B. Yamada, F. Oku, T. Harada. *J. Polym. Sci.: Part A: Polym. Chem.* **2003**, *41*, 645-654.
11. R. McHale, F. Aldabbagh, W. M. Carroll, B. Yamada. *Macromol. Chem. Phys.* **2005**, *206*, 2054-2066.
12. A. Matsumoto, T. Sumihara. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 288-296.
13. S. B. Choi, A. Takahara, N. Amaya, Y. Murata, T. Kajiyama. *Polym. J.* **1989**, *21*, 215-219.
14. K. Yamada, M. Takayanagi, Y. Murata. *Polymer* **1986**, *27*, 1054-1057.
15. A. Matsumoto, N. Maeo, E. Sato. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 2136-2147.
16. B. Yamada, E. Yoshikawa, K. Shiraishi, H. Miura, T. Otsu. *Polymer* **1991**, *32*, 1892-1896.
17. J. Villieras, M. Rambaud. *Synthesis* **1982**, *11*, 924-926.
18. K. J. Abbey, D. L. Trumbo, G. M. Carlson, M. J. Masola, R. A. Zander. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3417-3424.
19. E. Sato, I. Uehara, H. Horibe, A. Matsumoto. *Macromolecules* **2014**, *47*, 937-943.
20. M. Yoshioka, T. Otsu. *Macromolecules* **1992**, *25*, 559-562.
21. M. Yoshioka, T. Otsu. *Macromolecules* **1992**, *25*, 2599-2602.
22. E. Sato, P. B. Zetterlund, B. Yamada. *Macromolecules* **2004**, *37*, 2363-2370.
23. C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang. *Macromolecules* **1996**, *29*, 7717-7726.
24. D. Cochin, A. Laschewsky, N. Pantoustier. *Polymer* **2000**, *41*, 3895-3903.

Caption to Figures

Figure 1. ^1H NMR spectrum of PDiPF MM prepared in the presence of MBMA (run 4 in Table 1) after precipitation in methanol/water = 4/1 (vol./vol.).

Figure 2. ^1H NMR spectrum of PDiPF MM prepared in the presence of MMAD (run 10 in Table 1) after precipitation in methanol/water = 4/1 (vol./vol.). The peak indicated by an asterisk is due to water.

Figure 3. GPC elution curves for (a) PEA-g-PDiPF(MBMA) and (b) PEA-g-PDiPF(MMAD-1); the polymerization mixture (red solid line), the polymer after reprecipitation in acetone/hexane = 1/9 (vol./vol.) (blue dashed line), and PDiPF macromonomer (black dotted line).

Figure 4. ^1H NMR spectrum of the isolated PEA-g-PDiPF(MMAD-1). The peak indicated by an asterisk is due to water.

Figure 5. DSC curve of the isolated PEA-g-PDiPF(MMAD-2); (a) 1st heating, (b) 2nd heating, and (c) 1st cooling steps at 25 °C/min.

Figure 6. TG/DTA curves of the isolated PEA-g-PDiPF(MMAD-2) (black), PDiPF (red), and PEA (blue).

Figure 7. AFM images of spin coated film of the isolated PEA-g-PDiPF(MMAD-1) recorded by (a) height and (b) phase modes. The scanning area was 1 μm x 1 μm .

Figure 8. Transmittance of the isolated PEA-g-PDiPF(MMAD-1) cast film (film thickness = 110 μm).

Figure 9. Photographs of (a)(b) the isolated PEA-g-PDiPF(MMAD-1) and (c) PDiPF cast films.

Table 1. Results of the bulk polymerization of DiPF in the presence and absence of AFCT agents.

run	AFCT agent ^a	Temp. ^b (°C)	Time (h)	Conv. (%)	$M_{n, GPC} ; M_w/M_n$		$M_{n, NMR}$	$(M_{n, GPC}/M_{n, NMR}) \times 100$ (%)
					before precipitation	after precipitation ^c		
1	-	80	7	47.6	N.D. ^d	55,200; 1.31	-	-
2	MBMA	80	4	8.3	6,000; 1.68	8,600; 1.45	24,600	35
3	-	105	5	65.0	27,000; 2.16	28,400; 1.98	-	-
4	MBMA	105	5	7.4	5,700; 1.42	7,700; 1.32	22,100	35
5	-	128	5	62.4	13,600; 2.09	23,400; 1.63	-	-
6	MBMA	128	5	5.7	5,200; 1.50	7,700; 1.30	29,100	26
7	MMAD	128	5	19.4	3,500; 1.51	5,900; 1.23	11,100	54
8	-	148	5	56.9	3,900; 1.58	9,200; 1.42	-	-
9	MBMA	148	5	7.4	3,200; 1.26	6,100; 1.14	18,300	33
10	MMAD	148	2	13.0	2,100; 1.35	5,000; 1.11	6,900	72

^a[DiPF] : [MBMA] = 1000 : 1 and [DiPF] : [MMAD] = 50 : 1. ^b[MAIB] = 3.9 x 10⁻⁵ mol/L at 80 °C, [ACN] = 3.9 x 10⁻⁵ mol/L at 105 °C, [ATMP] = 9.4 x 10⁻⁴ mol/L at 128 °C, and [AMP] = 4.7 x 10⁻⁵ mol/L at 148 °C.

^cPrecipitated in the mixture of methanol/water (= 4/1 v/v). ^dNot determined.

Table 2. Results of graft copolymerization of EA and PDiPF MM.^a

Graft Copolymer	PDiPF MM			Graft Copolymer		
	$M_{n, \text{GPC}}$	M_w/M_n	$(M_{n, \text{GPC}}/M_{n, \text{NMR}}) \times 100 (\%)$	M_n	M_w/M_n	d[EA]/d[DiPF]
PEA-g-PDiPF(MBMA)	7,700	1.31	27	N.D. ^b	N.D. ^b	N.D. ^b
PEA-g-PDiPF(MMAD-1)	5,900	1.29	57	50,000 ^c	2.21 ^c	69/31 ^c
PEA-g-PDiPF(MMAD-2)	4,800	1.26	45	52,100 ^c	1.92 ^c	N.D. ^b

^a[DiPF unit in PDiPF MM] : [EA] : [AIBN] = 50 : 50 : 1, in toluene (45.4 wt%) at 65 °C for 48 h.

^bNot determined. ^cAfter precipitation in acetone/hexane = 1/9 (vol./vol.).

Chart 1. Structure of monomer and AFCT agents.

Scheme 1. (a) AFCT, (b) reinitiation, and (c) primary radical termination in radical polymerization of DiPF in the presence of AFCT agent.

Figure 1. ^1H NMR spectrum of PDiPF MM prepared in the presence of MBMA (run 4 in Table 1) after precipitation in methanol/water = 4/1 (vol./vol.).

Figure 2. ^1H NMR spectrum of PDiPF MM prepared in the presence of MMAD (run 10 in Table 1) after precipitation in methanol/water = 4/1 (vol./vol.). The peak indicated by an asterisk is due to water.

Figure 3. GPC elution curves for (a) PEA-*g*-PDiPF(MBMA) and (b) PEA-*g*-PDiPF(MMAD-1); the polymerization mixture (red solid line), the polymer after reprecipitation in acetone/hexane = 1/9 (vol./vol.) (blue dashed line), and PDiPF macromonomer (black dotted line).

Figure 4. ^1H NMR spectrum of the isolated PEA-g-PDiPF(MMAD-1). The peak indicated by an asterisk is due to water.

Figure 5. DSC curve of the isolated PEA-*g*-PDiPF(MMAD-2); (a) 1st heating, (b) 2nd heating, and (c) 1st cooling steps at 25 °C/min.

Figure 6. TG/DTA curves of the isolated PEA-g-PDiPF(MMAD-2) (black), PDiPF (red), and PEA (blue).

Figure 7. AFM images of spin coated film of the isolated PEA-*g*-PDiPF(MMAD-1) recorded by (a) height and (b) phase modes. The scanning area was 1 μm x 1 μm .

Figure 8. Transmittance of the isolated PEA-*g*-PDiPF(MMAD-1) cast film (film thickness = 110 μm).

Figure 9. Photographs of (a)(b) the isolated PEA-*g*-PDiPF(MMAD-1) and (c) PDiPF cast films.

GRAPHICAL ABSTRACT **Short text for the Table of Contents**

Graft copolymers consisting of rigid poly(diisopropyl fumarate) branches and a soft poly(ethyl acrylate) backbone were synthesized by full free radical polymerization process. 2,2-Dimethyl-4-methylene-pentanedioic acid dimethyl ester was found to be an efficient addition-fragmentation chain transfer agent for diisopropyl fumarate polymerization to generate poly(diisopropyl fumarate) macromonomer. Copolymerization of poly(diisopropyl fumarate) macromonomer with ethyl acrylate accomplished the generation of the graft copolymer having flexible backbone and rigid branches, which is transparent and shows a microphase separated structure.

Facile Synthesis of Graft Copolymers Containing Rigid Poly(dialkyl fumarate) Branches by Macromonomer Method

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Supporting Information

Figure S1. AFM images of the spin coated film of the polymer blend (PDiPF/PEA = 50/50 wt%) recorded by (a) height and (b) phase modes.