

RAFT-Mediated Radiation Grafting on Natural Fibers in Aqueous Emulsion †

Bin Jeremiah D. Barba ^{1,2,*} , David P. Peñaloza, Jr. ² , Noriaki Seko ³ and Jordan F. Madrid ¹

¹ Chemistry Research Section, Department of Science and Technology, Philippine Nuclear Research Institute, Quezon City 1101, Philippines; jfmadrid@pnri.dost.gov.ph

² Department of Chemistry, College of Science, De La Salle University Manila, Manila 0922, Philippines; david.penalozajr@dlsu.edu.ph

³ Quantum Beam Science Research Directorate, National Institutes for Quantum and Radiological Science and Technology (QST), Takasaki 370-1292, Japan; seko.noriaki@qst.go.jp

* Correspondence: bjdbarba@pnri.dost.gov.ph; Tel.: +63-289-296-011

† Presented at the 2nd International Online Conference on Polymer Science—Polymers and Nanotechnology for Industry 4.0, 1–15 November 2021; Available online: <https://iocps2021.sciforum.net/>.

Abstract: Using aqueous emulsion as the medium in radiation-induced graft polymerization (RIGP) offers an environment-friendly shift from organic solvents while increasing polymerization efficiency through known water radiolysis-based graft initiation. In the present paper, we further extend the applicability of RIGP in emulsion under the influence of reversible addition fragmentation chain transfer (RAFT) mechanisms. Emulsions prepared with Tween 20 showed good colloidal stability for several hours. Subjecting it to simultaneous irradiation with abaca fibers resulted in successful grafting, supported by gravimetric, IR, SEM, and TG analysis. A correlation was drawn between smaller monomer micelles and the enhancement of grafting driven by diffusion and surface area coverage. RAFT mechanisms were also conserved based on molecular weight evolution. RAFT-mediated RIGP in aqueous emulsion shows good potential as a versatile and green surface modification technique for natural fibers for various functional applications.



Citation: Barba, B.J.D.; Peñaloza, D.P., Jr.; Seko, N.; Madrid, J.F.

RAFT-Mediated Radiation Grafting on Natural Fibers in Aqueous Emulsion. *Mater. Proc.* **2021**, *7*, 4. <https://doi.org/10.3390/IOCP2021-11243>

Academic Editor: Shin-ichi Yusa

Published: 30 October 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: radiation-induced graft polymerization (RIGP); reversible addition fragmentation chain transfer (RAFT) polymerization; emulsion grafting; natural fibers

1. Introduction

Emulsion polymerization involves the free radical polymerization of monomer molecules in large and discrete polymer particles dispersed in a continuous aqueous phase stabilized by surfactants. This aids in the utilization of water as the solvent for relatively hydrophobic monomers contributing to green chemistry, as it significantly reduces organic solvent dependence and their corresponding VOC generation [1]. Due to the segregation of free radicals within the micelles formed in emulsions, the probability of bimolecular termination is reduced, leading to faster polymerization rates and higher molecular weights [2]. This technique has been successfully applied in various industries utilizing polymers that include coatings, adhesives, plastics, and synthetic rubber.

This has also been explored in graft copolymerization, particularly radiation-induced graft polymerization (RIGP). RIGP can be applied in the synthesis of functional materials as it involves the attachment of polymer chains with advantageous tailored properties to the surface of a base polymer with desirable bulk character. The general mechanism is illustrated in Figure 1 [3]. The key advantage here is that graft reactivity is usually higher in water due to its radiolytic products, which participate in the initiation phase [4]. Glycidyl methacrylate (GMA), a widely used monomer in RIGP, is only soluble in water at concentrations less than 2%. In a previous work [5], emulsifying GMA with Tween 20 formed a milky emulsion that was stable for 48 h and resulted in a sufficiently high grafting

yield on polyethylene fibers at doses as low as 10 kGy. GMA concentrations can reach up to 10% (*w/w*), which effectively enhances the degree of grafting [6,7].

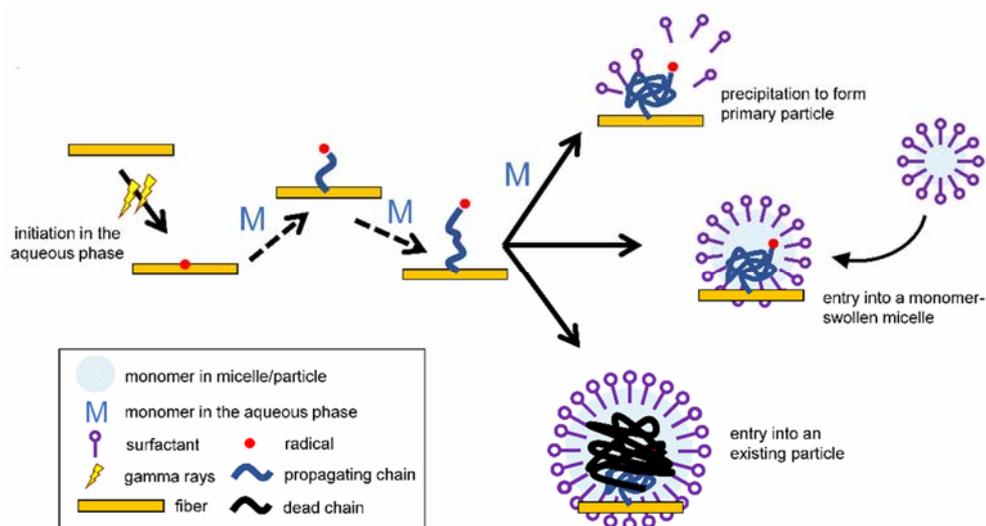


Figure 1. Proposed general mechanism of RIGP in emulsion [3].

In the preparation of diverse functional materials, control over polymer brush architecture leads to a significant influence over surface properties and often enhances its specific functionality [8]. Among controlled radical polymerization techniques, the reversible addition fragmentation chain transfer (RAFT) mechanism is applicable involving both radiation-initiated reactions and emulsion systems [9–11]. The RAFT agent, initially dissolved in the monomer before emulsification, is likely to be found inside the micelle, where it can mediate chain growth through a reversible deactivation of propagating chains [12]. Difficulties associated with the use of RAFT in *ab initio* emulsion systems, such as low polymerization rates, broad molecular weight distribution, and loss of control, are usually attributed to colloidal instability and RAFT transport [13]. In this work, RAFT-mediated radiation grafting in aqueous emulsion using Tween 20 as the surfactant for emulsion polymerization was assessed for its pseudo-living character and its potential as a green surface modification technique for natural fibers for various functional applications.

2. Materials and Methods

2.1. Emulsion Preparation

The emulsion was prepared with the following components by weight: 10% GMA (>95%, TCI, Tokyo, Japan), 0.2% 4-cyano-4-(carbonothioylthio)pentanoic acid (CPPA, 97%, Strem Chemicals Inc., Newburyport, MA, USA), and 0.5–2% Tween 20 (Kanto Chemical Co., Inc., Tokyo, Japan) in ultrapure water. The solution was homogenized at 6000 rpm for 10 min. Stability and micelle size were measured by dynamic light scattering using an FPAR 1000 particle size analyzer (Otsuka Electronics Co., Ltd., Osaka, Japan) at 25 °C.

2.2. Radiation Grafting of Abaca Fibers

Pre-weighed abaca woven fabrics ($1 \times 5 \text{ cm}^2$) and 8 g of the emulsion were placed in a glass vial and purged with N_2 gas. The vial was placed in a Co-60 gamma irradiation chamber and polymerization was carried out at a dose rate of 1 kGy/h (in air). The fabrics were washed several times with methanol and tetrahydrofuran (THF) and dried to constant weight, in vacuo. The homopolymers were then precipitated from the solution using methanol and weighed. The degree of grafting (DG, %) was calculated from the percent weight gain of the fabric, while conversion (%) was determined from the added weight of the collected homopolymer and weight gain of the fabric over the initial amount of

monomer in the vial. A sample of homopolymers was dissolved in THF and analyzed using gel permeation chromatography (Chromaster, Hitachi HighTech, Japan equipped with Shodex Asahipak GF-16 7B guard and two GF-7M columns). Polymethyl methacrylate standards were used.

2.3. Characterization

The abaca fabrics before and after RIGP were subjected to several characterization techniques. The chemical information of the fabrics was examined by a Frontier FTIR Spectrophotometer (Perkin Elmer, Japan) in attenuated total reflectance (ATR) mode with 4 cm^{-1} resolution. The morphology and elemental composition of the fabric surface were examined by scanning electron microscopy with an energy dispersive X-ray (SEM-EDX) taken by a Hitachi SU3500 scanning electron microscope (Hitachi HighTech, Tokyo, Japan), coupled with an X-Max EDX spectrometer (Horiba Ltd., Kyoto, Japan) at vacuum conditions and acceleration voltage of 50 Pa and 10 kV, respectively. All fabrics were gold coated using a JFC-1600 Auto Fine Coater (JEOL Ltd., Tokyo, Japan) prior to scanning. The thermal decomposition profile of the fabrics was examined using a TG/DTA 6200 Extar 6000 (Seiko Instruments Inc., Tokyo, Japan) under a nitrogen atmosphere using a 5 mm aluminum sample pan, with the following heating program: (1) 25–130 °C at 20 °C/min; (2) 130 °C for 10 min; and continuing to 550 °C at 10 °C/min.

3. Results and Discussion

In the mechanism of emulsion polymerization via RAFT, the formation of oligomers at the initial phase can dramatically reduce the chemical potential of the nucleated particle and lead to a large amount of monomer to transfer from droplets to these particles [14]. This phenomenon, known as superswelling, ultimately destabilizes the emulsion and often leads to a loss of control of polymerization associated with the formation of a colored layer or coagulum. The use of a relatively higher surfactant concentration, preferably nonionic like Tween 20 above its critical micelle concentration (CMC), has been known to circumvent superswelling [15]. High amounts of surfactant (at least greater than their CMC) also ensure that most of the monomers, as well as the RAFT agent are in the stable micelles ($<1\ \mu\text{m}$), which are considerably smaller than monomer droplets ($>1\ \mu\text{m}$). This also aids in the rapid transport of RAFT agent to the growing particles owing to the larger surface area of the micelles [11].

Emulsion systems with different surfactant-to-monomer ratios were observed. As seen in Figure 2a, the degree of grafting (DG) increased when the surfactant amount was changed from 0.5 to 1% and then proceeded to decrease at higher levels of Tween 20. DG seems to correlate inversely with the observed micelle size of the emulsion. Smaller micelles can cover a wider surface area of the trunk polymer leading to an enhanced grafting efficiency [5]. Furthermore, smaller micelles usually diffuse better throughout the solution allowing them greater access to the site of graft propagation [4,5,16]. Based on these results, the surfactant concentration was fixed to 1% in further experiments as it exhibited the highest DG. At this concentration, the emulsion remained in a milky state (Figure 2b) with no phase separation, and was relatively stable for at least 10 h.

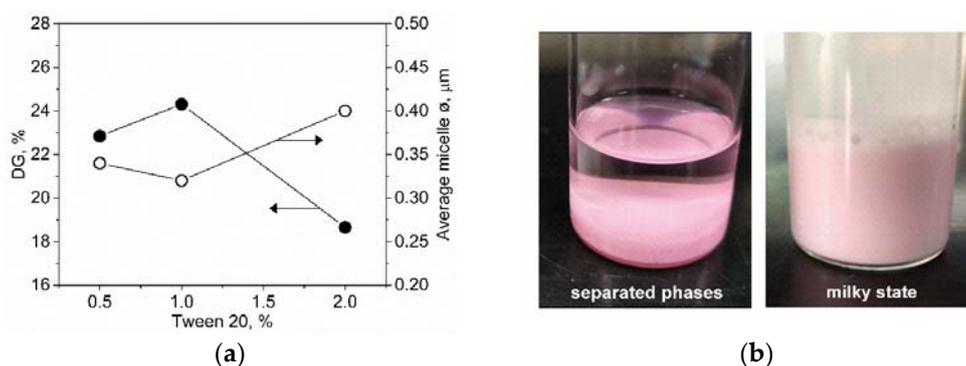


Figure 2. CTPA/GMA emulsion studies: (a) effect of surfactant concentration on the degree of grafting (DG) at 5 kGy absorbed dose and average micelle diameter $\bar{\phi}$; and (b) representative images of solution during initial separated phases and emulsified milky state.

Grafting in emulsion was further carried out at various absorbed doses. As seen in Figure 3a, there is an initial rapid increase in DG with the absorbed dose as it correlates to radical production. Continuous chain growth is also a feature of RAFT-mediated polymerization, which minimizes irreversible chain termination (dead chains) through the reversible deactivation of propagating polymer radicals (“living” chains) [17,18]. Therefore, grafted polymer chains continue to grow and contribute to the DG as long as monomers remain available. At higher absorbed doses, DG increase slowed down possibly due to the decrease in available monomer molecules during the course of the polymerization. This is reflected in the monomer conversion values shown in Figure 2b. Similarly, monomer conversion showed a rapid increase in the absorbed dose, then slowed down at higher doses due to restricted monomer diffusion with an increase in polymer concentration and viscosity. There was an initial linear increase in the conversion values as a function of absorbed dose, which translates to polymerization time (h) as the dose rate is fixed to 1 kGy/h. To estimate the properties of the grafted polymers in terms of molecular weight and polydispersity, GPC analysis was performed on the precipitated homopolymers from the solution. As reported in previous works on RAFT-mediated radiation-induced grafting, the growth of surface grafted polymer chains exists in dynamic equilibrium with the free polymer chains (homopolymers) formed in the grafting solution [9,19]. Figure 3c shows the chromatograms of PGMA homopolymers formed using conventional (without CPPA) and RAFT-mediated RIGP. In contrast to the former’s broad and multimodal molecular weight distribution, using RAFT polymerization demonstrated narrow and monomodal distribution with a polydispersity index of 1.35, and good correspondence with the calculated value based on the RAFT-monomer ratio and conversion [12]. These results suggest the pseudo-living characteristics of the polymerization, indicating that the RAFT mechanism was in effect in the emulsion [20].

Analyzing the fabrics using FTIR (Figure 4a), successful grafting is evident as supported by the appearance of C=O stretching bands at 1725 cm^{-1} and epoxide ring deformations at $750\text{--}950\text{ cm}^{-1}$, in addition to the cellulose profile of the fiber shown as peaks at 1600 , 1110 , and 1040 cm^{-1} , attributed to the glucose ring vibrations [21]. Figure 4b,c also show the extension of the degradation profile of abaca fiber after the cellulose main chain $250\text{--}360\text{ }^{\circ}\text{C}$ to $420\text{ }^{\circ}\text{C}$ attributed to the degradation of the grafted polymers [22]. Finally, the abaca fibers were examined using SEM-EDX. The pristine fiber showed a relatively smooth surface made of 60% carbon and 40% oxygen atoms (Figure 4d). Meanwhile, abaca-g-PGMA showed a much rougher surface due to the amorphous PGMA covalently grafted on its surface (Figure 4e). There is also an increase in the carbon content from the PGMA chain, shifting the composition to 70% C and 30% O. Trace amounts of sulfur (0.02%) were also detected which can be attributed to the thiocarbonylthio end of CPPA, which adds to the propagating chain during RAFT-mediated polymerization [9,12,18].

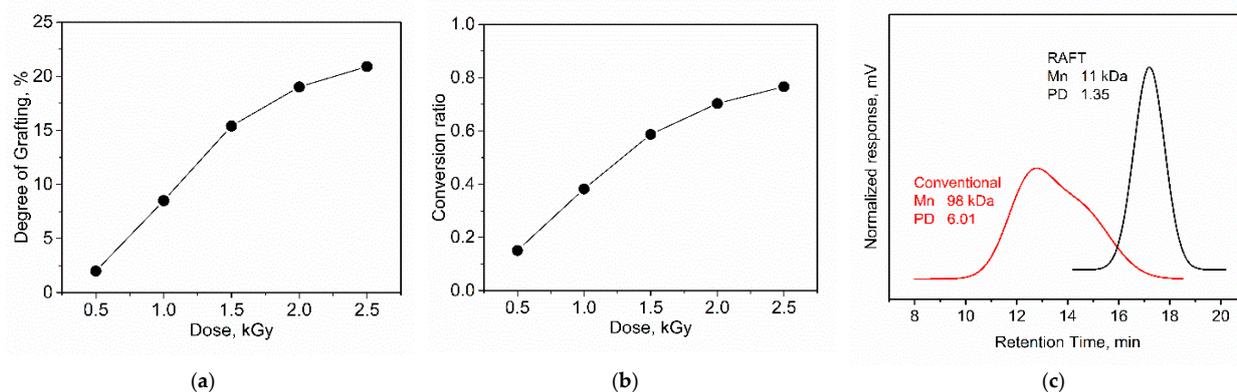


Figure 3. Effect of absorbed dose on the (a) degree of grafting and (b) monomer conversion; and (c) representative GPC chromatograms for PGMA formed using the conventional technique and with CPPA at ~0.8 conversion.

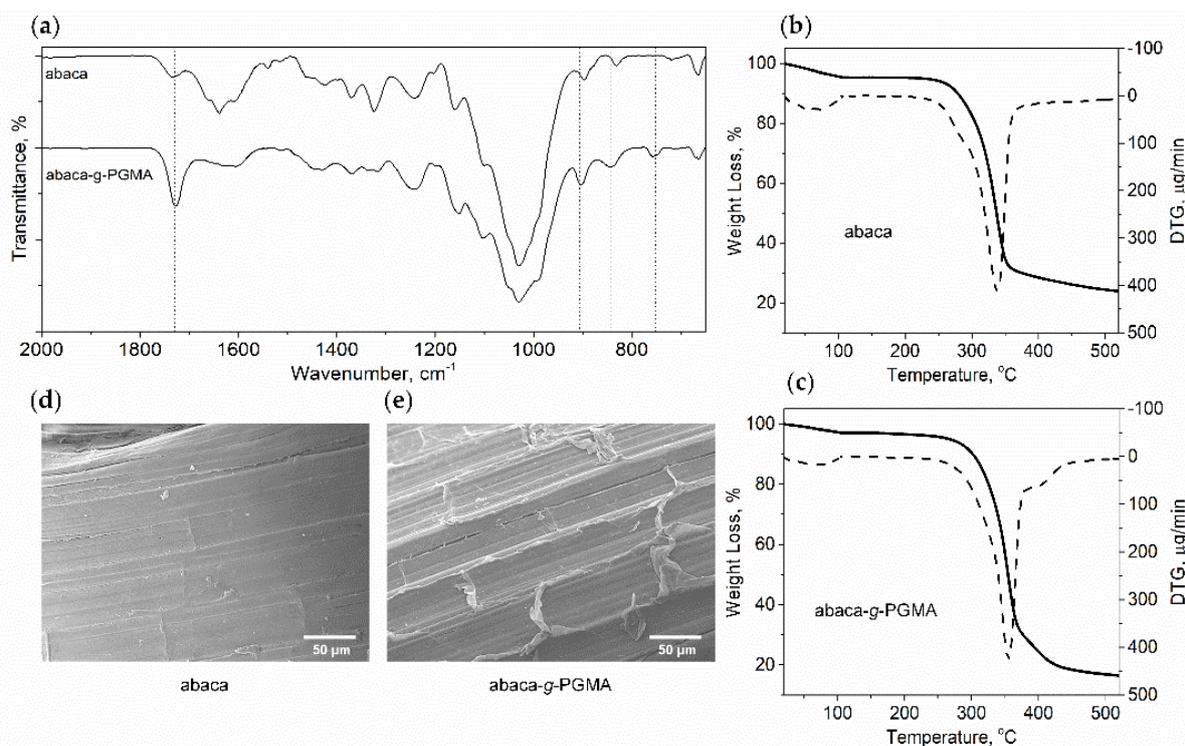


Figure 4. Evidence of grafting: (a) FTIR spectra highlighting the appearance of carbonyl and epoxide peaks on the (dashed lines); (b,c) weight loss and DTG (dashed lines) profiles; and (d,e) SEM micrograph of fiber surface of pristine and grafted abaca (DG, ~20%).

4. Conclusions

Graft polymerization reactions performed in aqueous emulsion offer an environment-friendly alternative to the use of organic solvents. In this work, glycidyl methacrylate was successfully grafted from abaca fibers using radiation-induced graft polymerization, mediated by reversible addition fragmentation chain transfer mechanism. Stable milky emulsions were formed using Tween 20 as the surfactant, and CPPA as the chain transfer agent. The emulsion remained stable for several hours and did not form an oily layer or coagulum indicative of unsuccessful RAFT polymerization. Instead, grafting proceeded with pseudo-living characteristics as supported by the increase in the degree of grafting with the linear increase in conversion, and the narrow and monomodal molecular weight distribution of generated homopolymers with good correspondence to the theoretic value.

Evidence of grafting was verified using FTIR, TGA, and SEM-EDX, which all showed the successful attachment of PGMA chains onto the abaca fiber. These results highlight the potential of RAFT-mediated RIGP in aqueous emulsion as a green surface modification technique for natural fibers. Studies on the further functionalization and characterization of the fibers for applications as adsorbents and composite reinforcement fillers are currently underway.

Author Contributions: Conceptualization, B.J.D.B., J.F.M. and D.P.P.J.; methodology, B.J.D.B., J.F.M. and N.S.; formal analysis, B.J.D.B.; investigation, B.J.D.B.; resources, N.S.; writing—original draft preparation, B.J.D.B.; writing—review and editing, J.F.M., D.P.P.J. and N.S.; supervision, J.F.M. and D.P.P.J. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors acknowledge the financial support given by the Department of Science and Technology—Science Education Institute (DOST-SEI), which sponsored the graduate scholarship and fellowship grant of Barba as part of their Human Resource Development Program. This work was also partially supported by JSPS KAKENHI (Grant No. JP17K05956). The authors also acknowledge the contributions of the Environment Polymer Group of QST-TARRI in providing assistance and facilities for the conduct of experiments.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhang, Y.; Dubé, M.A. *Green Emulsion Polymerization Technology BT—Polymer Reaction Engineering of Dispersed Systems: Volume I*; Pauer, W., Ed.; Springer International Publishing: Cham, Switzerland, 2018; pp. 65–100, ISBN 978-3-319-73479-8.
2. Chern, C.S. Emulsion polymerization mechanisms and kinetics. *Prog. Polym. Sci.* **2006**, *31*, 443–486. [[CrossRef](#)]
3. Lovell, P.A.; Schork, F.J. Fundamentals of Emulsion Polymerization. *Biomacromolecules* **2020**, *21*, 4396–4441. [[CrossRef](#)] [[PubMed](#)]
4. Wada, Y.; Tamada, M.; Seko, N.; Mitomo, H. Emulsion grafting of vinyl acetate onto preirradiated poly(3-hydroxybutyrate) film. *J. Appl. Polym. Sci.* **2008**, *107*, 2289–2294. [[CrossRef](#)]
5. Seko, N.; Bang, L.T.; Tamada, M. Syntheses of amine-type adsorbents with emulsion graft polymerization of glycidyl methacrylate. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* **2007**, *265*, 146–149. [[CrossRef](#)]
6. Madrid, J.F.; Lopez, G.E.P.; Abad, L.V. Application of full-factorial design in the synthesis of polypropylene-g-poly(glycidyl methacrylate) functional material for metal ion adsorption. *Radiat. Phys. Chem.* **2017**, *136*, 54–63. [[CrossRef](#)]
7. Madrid, J.F.; Ueki, Y.; Seko, N. Abaca/polyester nonwoven fabric functionalization for metal ion adsorbent synthesis via electron beam-induced emulsion grafting. *Radiat. Phys. Chem.* **2013**, *90*, 104–110. [[CrossRef](#)]
8. Feng, C.; Huang, X. Polymer Brushes: Efficient Synthesis and Applications. *Acc. Chem. Res.* **2018**, *51*, 2314–2323. [[CrossRef](#)] [[PubMed](#)]
9. Barsbay, M.; Güven, O.; Stenzel, M.H.; Davis, T.P.; Barner-Kowollik, C.; Barner, L. Verification of controlled grafting of styrene from cellulose via radiation-induced RAFT polymerization. *Macromolecules* **2007**, *40*, 7140–7147. [[CrossRef](#)]
10. Madrid, J.F.; Ueki, Y.; Abad, L.V.; Yamanobe, T.; Seko, N. RAFT-mediated graft polymerization of glycidyl methacrylate in emulsion from polyethylene/polypropylene initiated with γ -radiation. *J. Appl. Polym. Sci.* **2017**, *134*, 45270. [[CrossRef](#)]
11. Urbani, C.N.; Nguyen, H.N.; Monteiro, M.J. RAFT-Mediated Emulsion Polymerization of Styrene using a Non-Ionic Surfactant. *Aust. J. Chem.* **2006**, *59*, 728. [[CrossRef](#)]
12. Perrier, S. 50th Anniversary Perspective: RAFT Polymerization—A User Guide. *Macromolecules* **2017**, *50*, 7433–7447. [[CrossRef](#)]
13. Prescott, S.W.; Ballard, M.J.; Rizzardo, E.; Gilbert, R.G. RAFT in Emulsion Polymerization: What Makes it Different? *Aust. J. Chem.* **2002**, *55*, 415–424. [[CrossRef](#)]
14. Luo, Y.; Tsavalas, J.; Schork, F.J. Theoretical aspects of particle swelling in living free radical miniemulsion polymerization. *Macromolecules* **2001**, *34*, 5501–5507. [[CrossRef](#)]
15. Luo, Y.; Cui, X. Reversible addition–fragmentation chain transfer polymerization of methyl methacrylate in emulsion. *J. Polym. Sci. Part A Polym. Chem.* **2006**, *44*, 2837–2847. [[CrossRef](#)]
16. Ma, H.; Morita, K.; Hoshina, H.; Seko, N. Synthesis of Amine-type Adsorbents with Emulsion Graft Polymerization of 4-hydroxybutyl Acrylate Glycidylether. *Mater. Sci. Appl.* **2011**, *2*, 776–784. [[CrossRef](#)]
17. Moad, G.; Barner-Kowollik, C. The Mechanism and Kinetics of the RAFT Process: Overview, Rates, Stabilities, Side Reactions, Product Spectrum and Outstanding Challenges. In *Handbook of RAFT Polymerization*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2008; pp. 51–104.

18. Barner, L.; Zwaneveld, N.; Perera, S.; Pham, Y.; Davis, T.P. Reversible addition–fragmentation chain-transfer graft polymerization of styrene: Solid phases for organic and peptide synthesis. *J. Polym. Sci. Part A Polym. Chem.* **2002**, *40*, 4180–4192. [[CrossRef](#)]
19. Li, Y.; Schadler, L.S.; Benicewicz, B.C. Surface and particle modification via the RAFT process: Approach and properties. In *Handbook of RAFT Polymerization*; Wiley Online Library: Hoboken, NJ, USA, 2008.
20. Madrid, J.F.; Barsbay, M.; Abad, L.; Güven, O. Grafting of N, N-dimethylaminoethyl methacrylate from PE/PP nonwoven fabric via radiation-induced RAFT polymerization and quaternization of the grafts. *Radiat. Phys. Chem.* **2016**, *124*, 145–154. [[CrossRef](#)]
21. Sharif, J.; Mohamad, S.F.; Fatimah Othman, N.A.; Bakaruddin, N.A.; Osman, H.N.; Güven, O. Graft copolymerization of glycidyl methacrylate onto delignified kenaf fibers through pre-irradiation technique. *Radiat. Phys. Chem.* **2013**, *91*, 125–131. [[CrossRef](#)]
22. Ananthalakshmi, N.R.; Wadgaonkar, P.P.; Sivaram, S.; Varma, I.K. Thermal behaviour of glycidyl methacrylate homopolymers and copolymers. *J. Therm. Anal. Calorim.* **1999**, *58*, 533–539. [[CrossRef](#)]