Radical Living Graft Polymerization on the Surface of Polymeric Materials

Wantai Yang[†] **and Bengt Rånby***

Department of Polymer Technology, Royal Institute of Technology, 10044 Stockholm, Sweden

Received October 18, 1995
Revised Manuscript Received February 2, 1996

Introduction

Well-defined polymers and copolymers (e.g., block, graft) are usually prepared in a living polymeric system in which transfer and termination reactions are absent. For radical polymerization, the main difficulty to realize a "living process" is the bimolecular termination reaction by radical coupling or disproportionation. Because termination is a second-order reaction and propagation is first order of growing chain radicals, the proportion of termination increases with the concentration of free radicals. However, low concentration of growing radicals favors formation of high molecular mass polymers with no control of molecular weight and polydispersity. A recent breakthrough in the development of "radical living polymerization" is the invention of the reversible deactivation of growing radicals by coupling with a stable free radical or scavenger.[1−3]

Twenty-five years ago, Braun et al. studied the reactivity of aromatic pinacols as initiator.[4] Ten years later, they reported the synthesis of oligomers of methyl methacrylate (MMA) with two phenoxydiphenylmethyl end groups using 1,1,2,2-tetraphenyl-1,2-diphenoxyethane as initiator. They pointed out that these telechelic compounds are effective initiators of further free radical polymerization of vinyl monomers.[5]

Enlightened by these precursory results and combined with the practice of photografting polymerizations which have been initiated and carried out for more than 10 years in our laboratory,[6−8] we designed the present work. The intention is to implant "radical living polymerization" onto the surface-grafting polymerization. The experimental program contains two parts: The first is to synthesize end groups which are structurally similar to the ones reported (**4** and **5**) on the surface of polymer film by the known photografting method, and the second is to identify the reactivity of these end groups by photo- and thermoactivating polymerizations. As a result, a new macromolecular architecture, surface-grafted block copolymer, can be obtained by this method.

As an experimental process, the surface-grafting system presented here has the following advantages. (1) In comparison with solution and bulk polymerization systems, the growing radicals rooted on the polymer surface are not easily terminated by bimolecular reactions due to the limitation of a solid surface to which the chains are bonded, the low free radical concentration, and the low mobility. Therefore, the surface-grafting polymerization is expected to favor "living polymerization" with process control. (2) A living or controlled polymerization system, in general, is characterized by the linear relationship of the conversion of monomer and the molecular mass of polymer formed and also the polydispersity of the polymer when a fast initiation process comparatively with the propagation rate is concerned. In the surface-grafting polymerization, with the living end groups bound chemically on the surface of polymer, we can follow the polymerization process by measuring the increase in weight of the substrate.

Experimental Section

Polymer Substrate and Chemicals. Commercial LDPE film with 63 μm thickness was used as substrate to be grafted. Benzophenone (BP), xanthone, and 9-fluorenone (from Aldrich) were used as photoinitiators. Acrylic acid (AA) inhibited with 200 ppm hydroquinone monomethyl ether, methacrylic acid (MAA) inhibited with 250 ppm hydroquinine, and styrene (St) inhibited with 10−15 ppm 4-*tert*-butylcatechol were used as monomers. All chemicals were used as supplied without further purification.

Surface Photografting of Living End Groups. A solution of monomer and photoinitiator, e.g., MAA and BP (5 wt %), was applied by a microsyringe between two LDPE films (50 × 50 mm), and the thickness of the solution layer was controlled to around 5 μm. The assembly with a clear quartz plate on top was irradiated for 1 min at 55 °C with a 2 kW high-pressure mercury lamp (HPM 15, from Philips) at a distance of 15 cm from the lamp to the assembly. After immersion of the photografted laminate in a proper solvent, e.g., hot water (80 °C) when MAA was used as monomer, the two LDPE films could be separated. In this way two films, each with a layer-grafted polymer on one side, were obtained. Then acetone was used for removing unreacted monomer and photoinitiator, and homopolymers were removed by extraction (PAA and PMAA by water, PSt by ethyl acetate).

Photoactivating Polymerization. The photoactivating polymerization was carried out with the same polymerization procedure as in the photografting section except that only pure monomer was applied. The percent conversion of monomer AA or MAA is the ratio of the weight of the polymer formed and the weight of the monomer added. The unreacted monomer was removed by evaporation. Grafting efficiency of MAA or AA is the percentage of the grafted polymer on the surface of the LDPE film of the whole amount of polymer formed. W_g is the weight increase of the LDPE film from the grafted polymer. Homopolymer was separated from the grafted polymer by extraction with water as solvent.

Thermoactivating Polymerization. Thermoactivating polymerization was carried out in a solution of MAA or AA (80 mL) and water (80 mL). After 15 min of purging by nitrogen gas, the film with living end groups was placed in the solution, and the polymerization temperature was kept at 85 °C. The polymerization process was monitored by measuring the weight increase (W_g) of the film after washing with hot water and drying versus the polymerization time.

Results and Discussion

Introduction of Living End Groups. In a series of studies,[9] we have concluded that benzophenone, xanthone, and 9-fluorenone preferentially undergo a hydrogen abstraction reaction from an H-donor, e.g., the surface of the LDPE film under the irradiation of far-UV light (200−300 nm). A grafting polymerization is initiated when monomers are present as shown in reactions 1−4. It has been found that the termination reaction of this graft system[10] is mainly by combination of growing chain radicals and semipinacol radicals, i.e., reaction 6 rather than reactions 5 and 7.

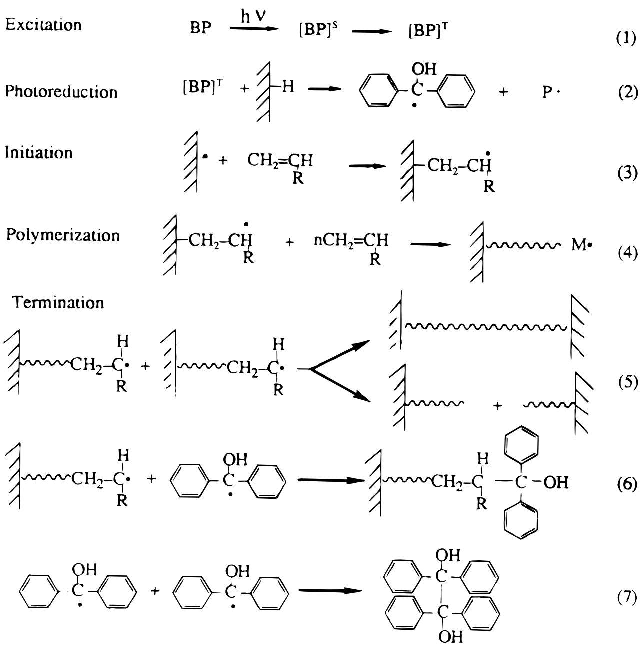
This termination pattern produces a special grafted copolymer which is rooted on the surface of the polymer substrates and carries end groups which are expected to initiate a radical polymerization due to their similarity to the phenoxydiphenylmethyl end groups (**5**) at the ends of grafted chains. According to this principle, we have synthesized five functional films (labeled as **I**−**V**)

---

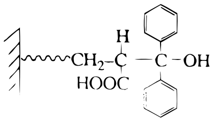
* To whom correspondence should be addressed.

[†] Visiting scientist from Beijing University of Chemical Technology, Beijing 100029, People's Republic of China.

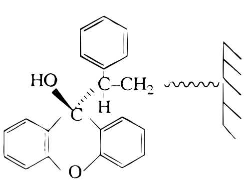
0024-9297/96/2229-3308$12.00/0



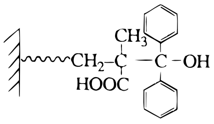
with different end groups by grafting three different monomers (acrylic acid, methacrylic acid, and styrene) with these photoinitiators (benzophenone, xanthone, and 9-fluorenone). The chemical structures are as follows:



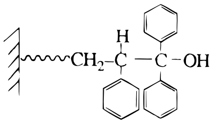
(I)



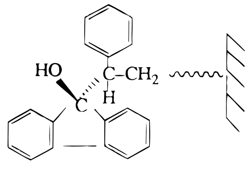
(IV)



(II)



(III)



(V)

Photoactivating Polymerization. The photoinitiating reaction of the five kinds of end groups (**I**−**V**) with acrylic acid and methacrylic acid as monomers was studied, and the results are given in Table 1 and Figure 1. It is seen that all these end groups except for **I** consisting of acrylic acid and benzophenone can reinitiate polymerization of methacrylic acid under UV irradiation. Since the absolute number of the grafted polymer end groups of the functional films was not measured, we cannot compare quantitatively the reactivity of the five end groups at this time. The data in Figure 1 were obtained by a process of repeated addition of pure monomer to the active layer between the two films with the functional groups. A linear relationship is observed at the early part of the polymerization. The deviation from the linearity after three or four additions of pure monomer is probably due to homopolymerization initiated by the semipinacol free radicals and the screening effect of UV light absorption by the gradually thicker film.

Table 1. Performance of Five Living End Groups in Photopolymerization

type of end groups	monomer	irradiation time (s)	temperature (°C)	conversion (%)	grafting efficiency (%)
I	MAA	60	50	3	
II	MAA	60	50	76	80
III	MAA	60	50	45	86
IV	MAA	60	50	51	93
V	MAA	60	50	40	80

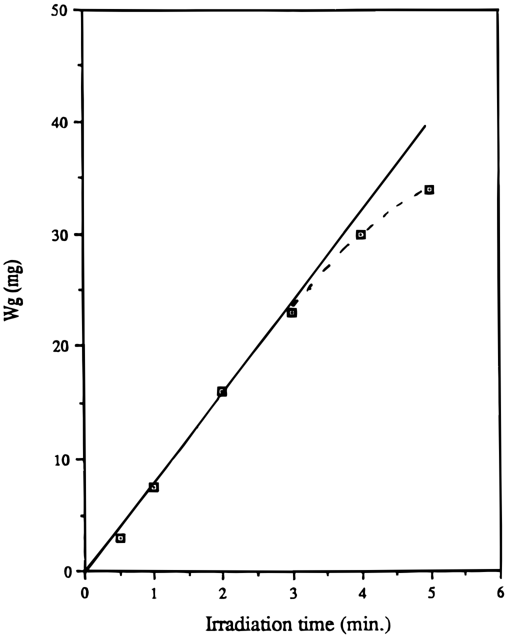


Figure 1. Relationship of the weight increase (W_g) of the LDPE functional film **II** and the UV irradiation time at 50 °C with MAA as monomer.

Thermal Activating Polymerization. In order to eliminate the possible interference of residual photoinitiator, we also tested the performance of the active end groups in initiating radical polymerization without UV irradiation. When a solution polymerization with the functional films as initiators is initiated by elevating the reaction temperature, the following results are expected. (i) The residual photoinitiators used in the photografting stage have low reactivity to initiate a thermal radical polymerization at the polymerization temperature used. (ii) Even though residual photoinitiators or other byproducts generated in the photografting stage, e.g., pinacol, have some initiation reactivity, they can only result in the formation of homopolymer which is easily separated from the grafted polymer or the substrates. (iii) Only polymerization initiated by the end groups are connected chemically to polymer substrate and can increase the weight of the functional films.

The initiating efficiency of the five functional films in the thermal polymerization system is given in Table 2. The significant weight increases of the substrate films show that the end groups of the grafted chains do have a reinitiating reactivity, and the effects are not the results of residual photoinitiators.

The weight increase of the LDPE films versus polymerization time is plotted in Figure 2. The growth curves in Figure 2 can be divided into two parts, a transient or early period and a linear or stable period. We postulate that the transient period is the initiating stage and the linear period the "living polymerization

Table 2. Performance of the Five End Groups in Thermal Activating Polymerization

type of end groups	monomer	temperature (°C)	polymerization time (h)	weight increase of LDPE film (mg)[a]
I	MAA	85	2	54
I	AA	85	3	30
II	MAA	85	2	70
III	MAA	85	3	160
III	AA	85	3	94
IV	MAA	85	3	550
IV	AA	85	3	110

[a] The original weight of each LDPE film was about 250 mg.

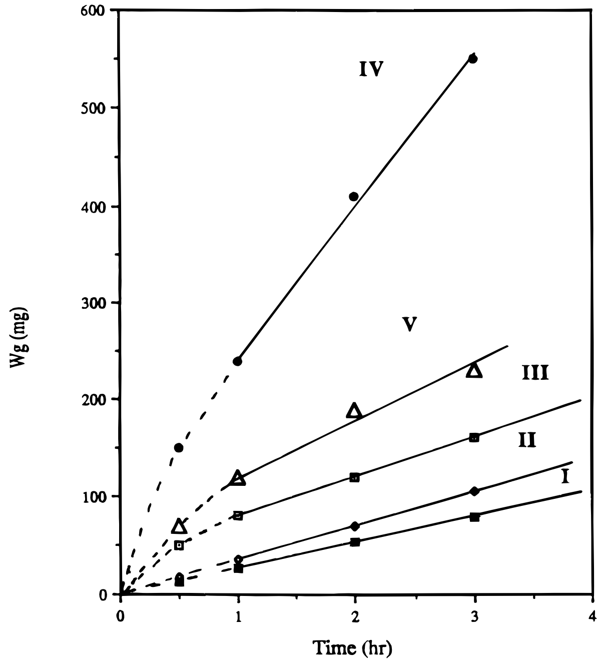


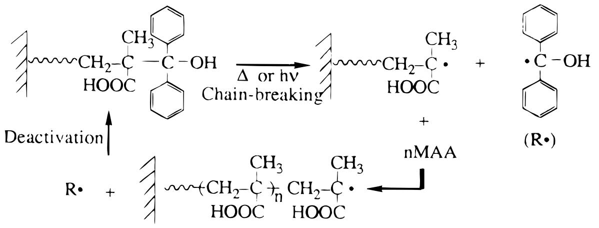
Figure 2. Relationship of the weight increase (W_g) of the five functional LDPE films **I**–**V** and the polymerization time at 85 °C with MAA as monomer. Each LDPE film weighed about 250 mg.

period". According to this assumption, the differences of the five end groups (**I**–**V**) in the transient period can be interpreted as due to their initiating reactivities.

A. **III**–**V** formed by styrene with benzophenone, xanthone, and 9-fluorenone, respectively, have higher reactivity than the new end groups formed by methacrylic acid and the corresponding initiators. Therefore all three have great slopes at the early part of the polymerization and subsequently decrease to a stable propagation stage. B. **II** has the same end group as the one formed. Therefore, no transient period is observed. C. **I** has lower reactivity than that of the new end group formed due to the absence of an activation effect of the methyl group. Therefore it shows a negative effect.

For a living polymerization system, two important aspects often are taken as standards. One is conceptually the intrinsic properties such as life-time and reinitiating ability. Another is the property of the polymer produced such as the macromolecular mass and the molecular mass distribution. With the present experimental system, despite the fact that we did not have sufficient information about the grafted macromolecules growing gradually from the surface of the LDPE film, we think it is reasonable to assume the reinitiating ability of these end groups, which again and again polymerize acrylic monomers, i.e., they have the characteristics of a living end group which linearly increases the weight of the LDPE film. This means that the molecular mass and the mass distribution are controlled.

Based on these results and considerations, an analogous mechanism to that of a typical radical living polymerization can be written as follows with the **II**–methacrylic acid system as an example:



Acknowledgment. We are very grateful to Prof. Jean M. J. Fréchet for his enlightening lectures on polymer chemistry, especially for the information and creative instructions on "radical living polymerization", and to the Carl Trygger Foundation for finacial support.

References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* **1994**, *27*, 7228–7229.
(2) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 1185–1186.
(3) Doi, T.; Matsumoto, A.; Otsu, T. *J. Polym. Sci., A Polym. Chem. Ed.* **1994**, *32*, 2911–2918.
(4) Braun, D.; Becker, K. H. *Makromol. Chem.* **1971**, *147*, 91–99.
(5) Btedzki, A.; Braun, D. *Makromol. Chem.* **1981**, *182*, 1047–1056.
(6) Rånby, B.; Gao, Z. M.; Hult, A.; Zhang, P. Y. *Polym. Prepr. (ACS)* **1986**, *27:2*, *38*; *ACS Symp. Ser.* **1988**, *364*, 168.
(7) Zhang, P. Y.; Rånby, B. *J. Appl. Polym. Sci.* **1990**, *40*, 1647.
(8) Feng, Z. G.; Rånby, B. *Angew. Makromol. Chem.* **1992**, *195*, 17.
(9) Yang, W. T.; Rånby, B. Submitted to *Eur. Polym. J.* **1996**.
(10) Yang, W. T.; Rånby, B. Submitted to *J. Appl. Polym. Sci.* **1996**.

MA9515543