ELSEVIER

Polymer 40 (1999) 4515–4520

polymer

Synthesis of EPDM-g-PMMA through atom transfer radical polymerization

Xiao-song Wang, Ning Luo, Sheng-kang Ying*

Lab of Living Polymerization, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, People's Republic of China

Received 25 January 1998; received in revised form 21 September 1998; accepted 21 September 1998

Abstract

A new method to prepare the graft copolymers that have an ethylene-propylene-diene terpolymer (EPDM) rubber backbone and poly(methyl methacrylate) (PMMA) branches was described. Firstly, the brominated EPDM (EPDM-Br) was produced by the reaction between the EPDM and N-bromosuccinimide(NBS), then the EPDM-g-PMMA was created by the ATRP of MMA initiated by EPDM-Br in the presence of CuBr/bpy at 90°C. The study shows that the free radical transfer grafting polymerization does not existed in the ATRP of MMA initiated by allyl bromide/CuBr/bpy in the presence of pure EPDM. The propagation of the PMMA graft chains are in situ initiated by EPDM radicals which is created through the reaction between the EPDM-Br and CuBr. Moreover, the reaction conditions, such as solvent, reaction time, molar ratio of EPDM-Br : CuBr : bpy, were examined. The maximum graft efficiency(93%) was obtained at 90°C for 20 h, when the ratio of EPDM-Br : CuBr : bpy was 1 : 0.8 : 2.4. The graft copolymers were characterized by solvent extraction, IR and H^1-NMR spectra technique. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: ATRP; EPDM; Graft-from reaction

1. Introduction

The graft copolymer of the ethylene-propylene-diene terpolymer (EPDM)with the second polymer containing functional groups, such as PMMA, could dramatically increase the interaction of EPDM to a broad range of materials. The graft copolymer could be used as compatibilizers for polymer blends and composites.

Earlier attempts to prepare the EPDM graft polymers by free radical [1,2] or radiation [3-5] ''graft-from'' [6] as well as ''graft-onto'' [7] methods have always resulted in ill-defined products as a result of gel formation, backbone degradation, or simultaneous formation of homopolymer.

Cationic pathway has been used to get graft copolymer with well-controlled structure [8]. Besides the stringent conditions required for cationic polymerization, e.g., complete absence of water, the major draw back to the system is the limited scope of monomers. So this method can not be used in the synthesis of the EPDM-g-PMMA. In contrast, the controlled free radical polymerization is combination of the ease of polymerization and the large number of monomers capable of reaction. So the EPDM graft copolymers with well-controlled structure can be easily synthesized through controlled radical polymerization.

Some transition metal species complex by suitable ligand(s), M_t^n/L_x, e.g., CuX (X = Cl, Br)/2,2'-bipyridine(bpy), in conjunction with suitable alkyl halide, R-X (X = Cl and Br), can efficiently initiate the Atom Transfer Radical Polymerization (ATRP) of a large variety of olefins, e.g., styrene(St), methyl methacrylate (MMA) and methacrylate (MA). ATRP has been considered as a controlled free radical polymerization. For example, the R-Cl/CuCl/bpy system initiates the ATRP of styrene by the following mechanism [9].

By extension of this mechanism, various graft copolymers have been accomplished using suitable brominated polymer initiators (Polymer-Br) [10,11].

In order to get EPDM-g-PMMA, the EPDM backbone is brominated with N-bromosuccinimide (NBS) to introduce allyl bromine on the backbone and then the brominated backbone (EPDM-Br) is used in conjunction with CuBr/bpy to initiate the polymerization of MMA. Fig. 3 summarizes the principle stages of our study in this paper.

---

* Corresponding author. Tel.: + (021)-64253018; fax: + (021)-64236718.

PII: S0032-3861(98)00693-4

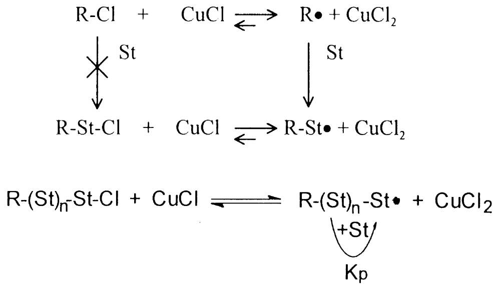

Fig. 1. The Mechanism of ATRP.

2. Experimental

2.1. Instrument and materials

All ^{1}H-NMR were recorded on a JEOL FX-90Q spectrophotometer. Infrared (IR) spectra were recorded on a Nicolet Magna-IR 550 spectrophotometer. Molecular weight and molecular weight distribution were measured using Waters 150C-ALC/GPC with Waters Styragel® HT_2, Styragel® HT_4 columns. The calibrated molecular weight was obtained by using a correction factor(0.56) with polystyrene standards.

A commercial EPDM rubber, Vistollon 2727, was obtained from Exxon Chemical Company. The rubber was purified by the solution-precipitation process using toluene as solvent and acetone as precipitant. NBS was received from WuLian Chem. Factory, China. Methyl methylacrylate was vacuum distilled from CaH_2 before polymerization. CuBr were purified according to the published procedure [12]. 2,2’-bipydridyl (bpy) were recrystallised from acetone. Allyl bromide was obtained from the Xing Hua Living Material Institute, and used as received.

2.2. Allylic bromination of EPDM

Ten grams of the EPDM rubber was dissolved in 500 ml CCl_4. The bromination was carried out by adding 0.45 g (2.5 mmol) NBS and 0.06 g (0.36 mmol) AIBN to the solution. After reflux at 90°C for 1.5 h, the reaction system was cooled, filtered and then precipitated by methanol. The resulted product was dried in a vacuum oven at 60°C for 20 h, and used for graft-from reaction to prepare the EPDM graft copolymers. The content of bromine in the EPDM-Br was analyzed by oxygen-bomb method.

2.3. Graft-from reaction

The graft polymerization was carried out in a previously dried glass tube equipped with a magnetic stirring bar under Ar. A typical experiment of the polymerization is given below: The EPDM-Br and solvent were put into the glass tube. After complete soluble, the CuBr, bpy and MMA were added. Then the reaction system was bubbled by Ar for 20 min. Finally, the mixture was stirred at 90°C under Ar.

After the heating was stopped, the reaction mixture was precipitated into methanol containing small amount HCl, and the precipitate were dried at 60°C for 8 h.

3. Results and discussion

3.1. Characterization of the graft copolymer

Isolation of the Graft Copolymer: The final product of the ATRP grafting polymerization may consist of ungrafted EPDM, EPDM-g-PMMA and PMMA homopolymer. The ungrafted EPDM and PMMA homopolymer can be separated from crude product by extraction using hexane and acetone, respectively. The hexane soluble fraction is almost identical with pure EPDM. However, the acetone soluble fraction usually contains both PMMA and EPDM with significantly high PMMA content [6]. In our experiment, there is almost no weight loss, when the product was extracted by hexane, which means all EPDM backbones are connected with the PMMA branch chain. However, the weight loss were observed, when the products were extracted using acetone, suggesting the homopolymer (PMMA) might be produced. The weights of the acetone soluble fractions of final products, which were varied under different conditions, were summarized in the tables below.

IR spectra of polymers: IR spectra of the films of the pure EPDM and isolated EPDM-g-PMMA cast from tetrahydrofuran (THF) solutions are shown in Fig. 4. The spectrum of the isolated graft copolymer shows an absorption band at 1730 cm^{-1} which is a characteristic peak of the $C = O$

Table 1
The results of the ATRP of MMA initiated by allyl bromide : CuBr : bpy = 1 : 1 : 3 with or without EPDM[a]

No.	EPDM/g	Solvents	Conv.(%)	Graft ratios(%)[b]	MW of PMMA[c]	
					$M_n \times 10^{-4}$	M_w/M_n
1	0	/	97	/	1.68	1.55
2	0	xylene	90	/	1.82	1.31
3	0.5	xylene	67	0	1.86	1.28
4	0.5	THF	63	0	1.36	1.16

[a] MMA: 8 ml solvent: 25 ml reaction temperature: 90°C reaction time: 8 h.

[b] Graft ratio = [(weight of acetone insoluble fraction in the final product) − (the weight of feeding EPDM)]/(weight of feeding EPDM)

[c] Acetone soluble fraction of the final product.

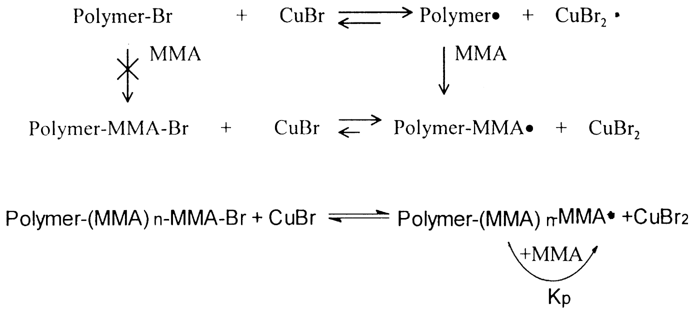

Fig. 2. The Mechanism of Graft Copolymerization through ATRP.

Table 2
The comparison of the Polymerization of MMA in EPDM-Br/CuBr/bpy and EPDM/CuBr/bpy systems [a]

No.	Initiating	System	Solvent	Time/hr	Total weight of the final product/g	Weight of fraction[b]	
	EPDM-Br / EPDM/g	–Br[c]:CuBr:bpy				soluble /g	insoluble /g
1	0.5/0	1 : 1 : 3	THF	20	2.122	1.710	0.412
2	0/0.5	0 : 1 : 3	THF	8	4.156	3.736	0.420
3	0.5/0	1 : 1 : 3	xylene	20	0.556	0.006	0.550
4	0/0.5	0 : 1 : 3	xylene	20	0.500	0	0.500
5	0.5/0	1 : 1 : 3	hexane	20	0.546	0.011	0.535

[a] Reaction temperature: 90°C, MMA: 8 ml, solvent:25 ml.
[b] The final products were extracted using acetone.
[c] Br: the total number of Br in feeding EPDM.

present in PMMA. It indicates that the PMMA is grafted to the EPDM.

NMR spectra of polymers: The ^{1}H-NMR spectra of the isolated graft copolymers show a peak at 3.6 ppm (Fig. 5), which is the characteristic peak of OCH_3. It is also indicates that the PMMA is grafted onto the EPDM. Moreover, the spectra show that the longer reaction time, the higher content of PMMA in the graft copolymer.

3.2. The possibility grafting through free radical transfer

The EPDM graft copolymers are usually obtained through the free radical polymerization of the vinyl monomers in the presence of EPDM [1,2], in which the radical centers are produced by the thermal decomposition of initiators, such as benzoyl peroxide and 2,2’-azobisisobutyronitrile, and then they are transferred to the EPDM backbones to form the PMMA grafting chains.

However, the radical centers in ATRP are produced by the reaction between the R-X and CuX and are controlled by the reversible equillium of the Cu(I)/Cu(II) redox process as described in Fig. 1. Therefore, the radical transfer reaction was retarded. Therefore, little EPDM-g-PMMA graft copolymer would be produced through the radical transfer grafting mechanism during the polymerization of MMA with allyl bromide/CuX/bpy in the presence of EPDM.

Table 1 shows the ATRP of MMA initiated by allyl bromide : CuBr : bpy = 1 : 1 : 3 in the bulk or in solution. In the experiments No. 1 and 2, the ATRP of MMA were

Table 3
Effect of –Br : CuBr : bpy ratio on the ATRP graft copolymerization[a]

No.	–Br[b] : CuBr : bpy	Total weight of the final products/g	Weight of fraction[c]	
			soluble/g	insoluble/g
1	1 : 0.8 : 2.4	0.5226	0.0016	0.5250
2	1 : 1 : 3	0.5560	0.0060	0.5500
3	1 : 1.5 : 4.5	0.6060	0.0210	0.5850

[a] EPDM-Br:0.5g, MMA:8 ml, xylene:25 ml, reac. temp.:90°C reac. time: 20 h.
[b] Br: the total number of Br in the feeding EPDM-Br.
[c] The final products were extracted using acetone.

Table 4
The effect of reaction time on the grafting reaction[a]

No.	Reac. time/hr	Weight of fraction[b]	
		soluble/g	insoluble/g
1	20	0.0060	0.5500
2	30	0.0334	0.6426
3	40	0.7056[c]	/

[a] EPCM-Br:0.5g, EPDM-Br : CuBr : Bpy = 1 : 1 : 3, MMA: 8 ml, xylene: 25 ml, reac. Temp.: 90°C.
[b] The final product was extracted using acetone.
[c] All of the final product dispersed in the acetone solution.

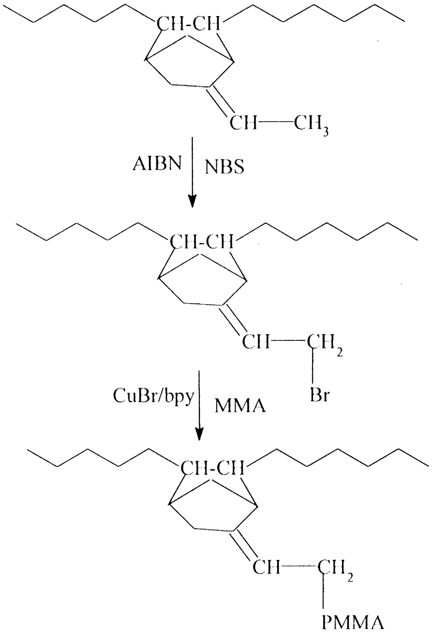

Fig. 3. The process of the Synthesis of EPDM-g-PMMA.

initiated by allyl bromide/CuBr/bpy without adding EPDM. The pure EPDM was fed in the experiments of Nos. 3 and 4 (Table 1) in order to examine the possibility of the free radical transfer grafting polymerization in ATRP.

As shown in Table 1, there are no graft copolymers produced in these systems. The ^{1}H-NMR spectrum of the acetone insoluble fraction of the final products of No. 3 in Table 1 is identical with the spectrum of pure EPDM. It further proved that no graft copolymer produced during the graft copolymerization.

Moreover, the phenomenon during the polymerizations of Nos. 3 and 4 in Table 1 also suggested no EPDM-g-PMMA formed. Phase separation was observed in the reaction systems with EPDM, when the stirring was stopped after reaction. The upper layer with green color was the solution of PMMA and the lower layer with yellow color was the solution of EPDM. It was caused by the different polarity of the PMMA homopolymer and the EPDM, they are not compatible without compatible agent, such as EPDM-g-PMMA.

The results discussed above indicate that the radical centers of the ATRP do not transfer to the EPDM backbone, which is different to the conventional radical grafting polymerization. The result may be caused by the lower radical concentration during the ATRP process [8] or the radical centers coordinated by the translation metal [13].

3.3. Initiating capability of EPDM-Br for the graft-from polymerization

When the EPDM-Br was used as a macroinitiator, the allyl bromine in the EPDM-Br would in situ react with CuBr/ bpy to produce polymeric radicals which could initiate the polymerization of MMA to form the graft PMMA chains as described in Fig. 2. It is the essential for graft-from polymerization.

To examine the initiating capability of EPDM-Br, the ATRP of MMA were carried out in the EPDM-Br/CuBr/ bpy systems (Nos. 3 and 5 in Table 2) in comparison with the polymerization of MMA in EPDM/ CuBr/ bpy (Nos. 2 and 4 in Table 2). When the EPDM was chosen instead of EPDM-Br, the polymerization system (EPDM/CuBr/bpy) was absence of any initiator for ATRP. The results were shown in Table 2.

As evidenced by lower yield recovered after a definite reaction time, the reaction rate of the system with EPDM-Br (No. 1 in Table 2) is slower than that of the system with

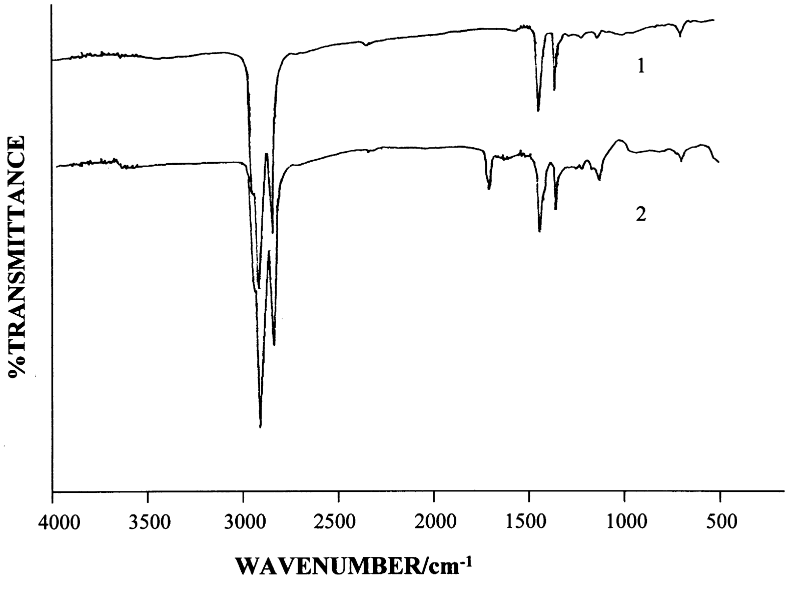

Fig. 4. IR Spectra of the Pure EPDM and EPDM-g-PMMA (1. Pure EPDM, 2. EPDM-g-PMMA).

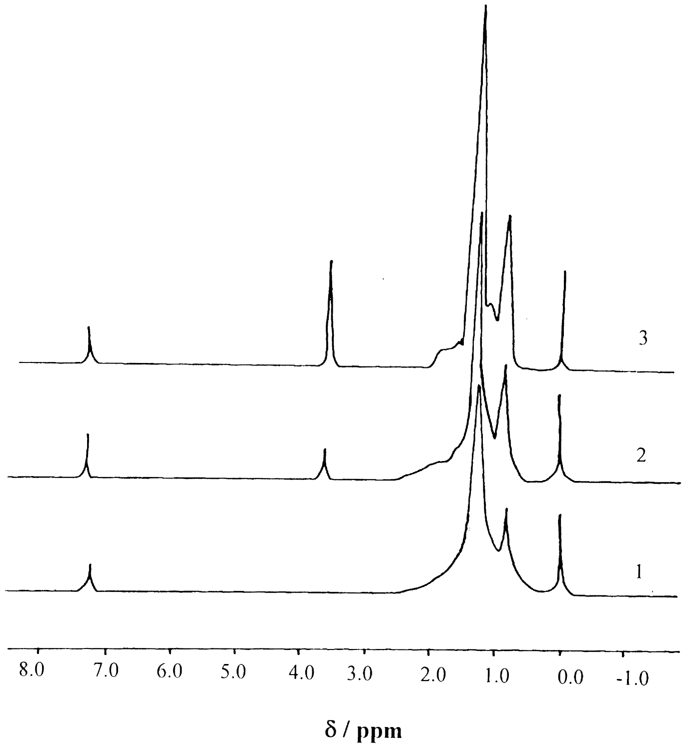

Fig. 5. ^{1}H-NMR Spectra of the Pure EPDM and Isolated EPDM-g-PMMA (Spectral conditions: solvent $CClD_3$, temperature 23°C, frequency 90 MHz. (1). Pure EPDM, (2). EPDM-g-PMMA after reaction for 7 h, 3. EPDM-g-PMMA after reaction for 20 h).

EPDM (No. 2 in Table 2) in the solvent of THF. It suggests that the free radical concentration in system with EPDM-Br is lower than that in system with pure EPDM, because the polymeric radical centers are controlled by the reversible equilibrium of the Cu(I)/Cu(II) redox process in the EPDM-Br system (Fig. 2). On the contrary, the radicals were produced by thermal initiating and were uncontrolled in the system with EPDM, which lead to higher concentration of free radical centers and more homopolymer obtained (evidenced by higher weight of acetone soluble fraction, No. 2 in Table 2).

When the xylene was chosen as solvent instead of THF, there was no polymer produced in the EPDM/CuBr/bpy system (No. 4 in Table 2), which suggests the thermal initiating is not occurred. It is different to the polymerization in the similar system in THF (No. 2 in Table 2), the reason will be researched further. However, the comparable reaction system with EPDM-Br(No. 3 in Table 2) produced the graft copolymer, which exactly proofed capability of EPDM-Br to initiate the ATRP graft-from polymerization.

Among the solvents, such as THF, xylene and hexane, used for the ATRP of MMA initiated by EPDM-Br, the graft efficiency is the highest in xylene. It is evidenced by the lowest weight of acetone fraction of final products (Table 2). It suggests that xylene is a suitable solvent for the grafting polymerization.

3.4. The effect of the molar ratio of –Br : CuBr : bpy on the graft from reaction

As shown in Table 3, when the molar ratio of CuBr relative to –Br (total number of Br in the feeding EPDM-Br) is increased, the weight of final product increased, and more homopolymer (as evidenced by the increasing of the weight of acetone soluble fraction in Table 3) is produced. It indicates that the reaction rate is accelerated and there is simultaneously a drop in the graft ratio owing to the higher concentration of free radical. It might be caused by the higher concentration of $[Cu^+]$ in the Cu(I)/Cu(II) redox system which shifts the equilibrium from the dormant species towards the active species (Fig. 2), and leading to the poor control of the radical active species.

Although NBS is an excellent allylic bromination agent, the side reaction cannot be avoided completely. For example, the agent would attack the double bond or substitute in the other positions except allylic position [14,15]. Thus the allylic bromination efficiency is usually about 90%. This means that when the feeding ratio of –Br : CuBr is 1 : 1, the molar ratio of allylic Br : CuBr is smaller than 1 : 1. This is why the grafting efficiency was the highest (as evidenced by the smallest weight of acetone-soluble fraction), when the feeding Br : CuBr : Bpy is 1 : 0.8 : 2.4 in which the radical center is better controlled.

3.5. The effect of reaction time

The effect of reaction time on the grafting copolymerization is shown in Table 4. The grafting copolymerization was carried out in xylene at 90°C with constant concentrations of EPDM-Br and CuBr/bpy. It was found that the grafting ratio increased, which is reflected by the increasing of the weight of acetone-insoluble fraction with extending the reaction time owing to the higher monomer conversion. When the final product obtained after 40 h extracted using acetone, the product all dispersed in acetone and the acetone solution become turbid. It suggests that longer PMMA chain formed, because of the limited grafting spots (the number of allyl Br in EPDM-Br) and the absence of transfer reaction as discussed above.

In conclusion, the EPDM-g-MMA has been synthesized though ATRP initiated by allylic brominated EPDM-Br. It provides a new way to synthesize graft copolymers with well-controlled structure.

Acknowledgements

This project was supported by National Natural Science Foundation of China (29634010-2), Shanghai Educational Development Foundation (SG97008).

References

[1] Park JY. J Appl Polym Sci 1994;51:1303.
[2] Morimoto M. J Appl Polym Sci 1981;26:261.
[3] Ranby B, Feng ZG. Polym prepr (Am Chem Soc Polym Chem) 1990;Div.31:446.
[4] Machi S, Silverman J. Proceedings Symposium on the Utilization of Large Radiation Sources to Accelerate Industrial Process. In: Large Radiation Sources in Industrial Process. 1969. p. 341.
[5] Machi S, Silverman J. Chem Abstr 1970;73:15681.
[6] Chung TC, Janrikul RB, Jiang GJ. Macromolecules 1994;27:26.
[7] Dean DB. J Appl Polym Sci 1986;32:5629.
[8] Kennedy P, Vidal A. J Polym Sci 1975;13:1765.
[9] Wang JS, Matyjaszewki K. J Am Chem Soc 1995;117(20):5614.
[10] Wang XS, Luo N, Ying SK. China Synthetic Rubber Industry 1997;20:117.
[11] Ying SK, Luo N, Wang XS. Chinese Patent Appl No 97 1 06314.2.
[12] Keller RN, Wycoff HD. Inorg Synth 1946;2:1.
[13] Wang XS, Luo N, Ying SK. Polymer Bulletin (China) accepted.
[14] Djerassi C. Chem Rev 1948;43:271.
[15] Rabjohn N. Organic synthesis Coll. Vol. IV, 921. New York: Wiley, 1963.