

Synthesis of novel functional polyolefin containing carboxylic acid via Friedel–Crafts acylation reaction

Yi Zheng^{a,b}, Yanguo Li^a, Li Pan^{a,b}, Yuesheng Li^{a,*}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China

^b Graduate School of the Chinese Academy of Sciences, Changchun 130022, China

Received 19 July 2006; received in revised form 17 September 2006; accepted 14 February 2007

Available online 16 February 2007

Dedicated to the memory of Professor Baotong Huang on the first anniversary of his death.

Abstract

The strong polar group, carboxylic acid, has triumphantly been introduced into ethylene and allylbenzene copolymers without obvious degradation or crosslinking via Friedel–Crafts (F–C) acylation reaction with glutaric anhydride (GA), succinic anhydride (SA) and phthalic anhydride (PA) in the presence of anhydrous aluminum chloride in carbon disulfide. Some important reaction parameters were examined in order to optimize the acylation process. In the optimum reaction conditions, almost all of the phenyls can be acylated with any anhydride. The microstructure of acylated copolymer was characterized by FT-IR, ¹H NMR and ¹H–¹H COSY. All the peaks of acylated copolymers can be accurately attributed, which indicates that all the acylation reactions occur only at the *para*-positions of the substituent of the aromatic rings. The thermal behavior was studied by differential scanning calorimetry (DSC), showing that the melting temperatures (*T*_ms) of acylated copolymers with GA firstly decrease slowly and then increase significantly with the increase of the amount of carboxyl acid groups. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Functionalization of polymers; Polyolefins; Friedel–Crafts acylation reaction

1. Introduction

Chemical and physical properties of polyolefins like adhesion, dyeability and compatibility with additives or polar polymers can be improved by incorporation of functional groups [1]. However, direct insertion-type copolymerization using polar comonomers is very difficult due to the Lewis acidity of heterogeneous Ziegler–Natta and homogeneous metallocene/aluminoxane catalysts [2]. Latest developments of late transition metal catalysts show much more improved tolerance against polar functionality due to the typically lower Lewis acidity, but they also suffer from the significant decrease of catalyst activity and polymer molecular weight because of the heteroatom (O, N, etc.)-containing functional groups [3]. As an alternative approach, by designing and synthesizing polyolefins containing

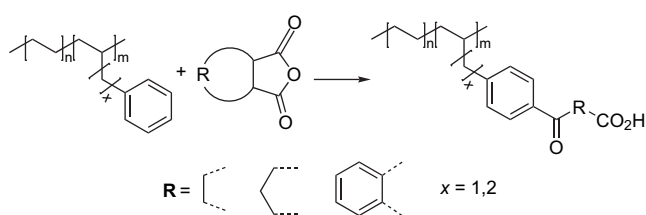
reactive groups that are free of catalyst-deactivating heteroatoms but very facile in functional transformation reactions, the functionalization of polyolefins by the reactive polyolefin “intermediate” is able to effectively avoid catalyst deactivation and produce functional polyolefins with well-defined molecular structures. To date, numerous studies have been carried out to introduce polar groups into nonpolar polyolefin by chemical modification such as a variety of functionalization reactions via dienes or borane comonomers with pendent double bonds [4]. Despite introducing polar groups, these modification reactions also have several drawbacks such as high cost, low conversion and multistep organic synthesis.

In contrast to the aliphatic hydrocarbons, which are inert to most chemical modifications, the activated aromatic units can undergo various electrophilic substitution reactions, such as nitration, sulfonation, halogenation, alkylation and so on [5]. So if phenyls are introduced into nonpolar polyolefins, a variety of modification reactions can be carried out. However, there

* Corresponding author. Tel.: +86 431 5695272; fax: +86 431 5685653.

E-mail address: ysli@ciac.jl.cn (Y. Li).

are only a few catalysts being capable of copolymerizing ethylene and styrene [6]. Some works have been done on chemical modification of olefin and substituent styrene copolymer [7]. However, in these works the pristine copolymers before modification are difficult to obtain with high molecular weight, and also the substituent styrenes commonly lie on the end of the copolymers for the chain transfer reaction in the copolymerization of ethylene and substituent styrene [8]. Therefore, we chose allylbenzene or 4-phenyl-1-butene instead of substituent styrenes as comonomer because they have outstanding virtues lie in the copolymerization is facile and common catalysts such as metallocenes and post-metallocenes can accomplish the copolymerization [9]. Metallocene and post-metallocene catalysts can play a great role in producing the reactive polyolefin “intermediate” with even distribution, high comonomer content and narrow molecular weight distributions [10]. In this article, we obtained the polyolefin “intermediate” containing reactive pendant phenyls by the copolymerization of ethylene and allylbenzene/4-phenyl-1-butene using *rac*-ethylenebis(indenyl)zirconium dichloride (*rac*-Et(Ind)₂ZrCl₂) as catalyst [11]. Then, carboxyl groups were introduced into pendant phenyls of the copolymers through a convenient yet highly efficient F–C acylation reaction (Scheme 1) [12]. This method not only overcomes the negative influence of using polar commoners in direct insertion-type copolymerization such as significantly reduced catalyst activity but also can be designed as new platforms for successive reactions [13]. The modified polyolefins bearing carboxyl and/or carbonyl groups have been widely applied in many fields. For example, they can be used as polar pigments and additives due to the compatibility with oxygen- and nitrogen-containing polymers. In addition, they can also be used to prepare macromolecule–metal complexes [14] and remove toxic metal ions from industrial effluent water supplies to avoid one of the major causes of water and soil pollutions because of the existence of coordination groups [15]. Hence, the polyolefins modified by acylation might also be used in the fields mentioned above. Unfortunately, there is only limited information about introducing carboxyls into aromatic rings and most of them are polystyrene polymers which are usually insoluble, so a precise characterization is difficult [16]. The modified copolymers we report here using different kinds of cyclic-anhydride are soluble, so the structure is unambiguously revealed by ¹H NMR and ¹H–¹H COSY spectral analyses. At the same time, a variety of reactive conditions have been investigated, if desired, almost all of the benzene groups can be acylated.



Scheme 1. F–C acylation reaction with different anhydride.

2. Experimental part

2.1. Materials

Ethylene and allylbenzene/4-phenyl-1-butene copolymers (3.85 and 6.45 pendant aromatic nuclei per 100 carbon atoms in the backbone, respectively) were prepared according to the procedures described in Ref. [9a] with minor modification. GA was distilled under vacuum, and carbon disulfide was dried overnight with calcium chloride, filtered and distilled prior to use. Anhydrous aluminum trichloride, SA and PA were purified by sublimation before use. All other chemicals were commercially available and used without further purification.

2.2. Acylation reaction

A typical reaction (entry 8 in Table 1) was carried out in a 250 ml three-necked round-bottom flask equipped with a condenser, a nitrogen inlet and a magnetic stirrer. After the flask was degassed and purged with nitrogen, carbon disulfide (40 ml) was added into the mixture of copolymer (0.5 g, 1.1 mmol pendant aromatic nuclei) and finely powdered anhydrous aluminum chloride (0.59 g, 4.4 mmol) in a water bath at 50 °C. The mixture was stirred for 10 min then GA (0.12 g, 1.1 mmol), which was sonicated in carbon disulfide (20 ml) to give a uniform suspension solution, was added to the mixture in a portion over 55 min, and the solution turned to dark red gradually. After the addition of GA solution in carbon disulfide was finished, the mixture was stirred for another 5 min. The reaction was quenched by the addition of ice water followed by dilute hydrochloric acid and then the product was thoroughly washed with water to remove any residual free acid. The concentrated organic phase was precipitated into ethanol, filtered and subsequently dried overnight under vacuum at 70 °C.

2.3. Characterization

¹H NMR and two-dimensional ¹H–¹H COSY spectra were recorded on a Varian Unity 400 MHz spectrometer at 100 °C using standard parameters. In both cases, 1,1,2,2-tetrachloroethane-*d*₂ was used as solvent and all chemical shifts were referred to the solvent shift at 5.94 ppm. The polymer films (0.5 mm) for the Fourier transform infrared (FT-IR) spectral analyses were prepared by melt pressing at 140 °C and the spectra were measured with a Bio-Red FTS-135 spectrophotometer. The melting temperatures (*T*_ms) of acylated copolymers were obtained by means of DSC with a Perkin–Elmer Pyris 1 Differential Scanning Calorimeter at a rate of 10 °C/min. *T*_m values reported in Table 1 were obtained from the second heating curve. The molecular weights and molecular weight distributions of the copolymers were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as solvent at a flow rate of 1.0 ml/min. The calibration was made with polystyrene standard EasiCal PS-1 (PL Ltd).

Table 1
Acylation of copolymers with anhydrides^a

Entry	Acyating agent	AlCl ₃ ^d	Temp (°C)	Time (h)	Yield (g)	Aromatic nuclei ^c	Carboxyl group ^c	M _w ^f (kg/mol)	M _w /M _n ^f	T _m ^g (°C)
1 ^b	—	—	—	—	—	6.45	—	58.7	3.25	126.6
2 ^b	GA	4	10	1	0.50	6.35	0.24	55.3	2.99	127.0
3 ^b	GA	4	30	1	0.45	3.43	1.46	47.6	2.78	128.0
4 ^b	GA	4	50	1	0.42	0.85	0.76	50.2	2.86	128.4
5 ^c	—	—	—	—	—	3.85	—	34.1	2.78	89.1
6 ^c	GA	4	10	1	0.49	3.76	0.18	32.8	2.24	88.8
7 ^c	GA	4	30	1	0.53	3.75	1.23	29.5	2.39	86.9
8 ^c	GA	4	50	1	0.57	3.57	2.96	27.6	2.59	91.7
9 ^c	GA	2	50	1	0.53	3.55	1.54	28.8	2.48	85.7
10 ^c	GA	6	50	1	0.59	3.53	3.07	27.4	2.52	93.7
11 ^c	GA	4	50	2	0.60	3.38	3.16	26.8	2.25	92.1
12 ^c	SA	4	50	1	0.57	3.70	3.42	29.5	2.37	93.4
13 ^c	SA	4	50	2	0.58	3.65	3.60	28.1	2.42	94.5
14 ^c	PA	4	50	1	0.60	3.80	2.52	30.5	2.52	88.9
15 ^c	PA	4	50	2	0.64	3.78	3.56	26.7	2.43	89.3

^a Reaction conditions: copolymer, 0.5 g; solvent, CS₂; total volume, 60 ml; [acyating agent]/[aromatic nuclei], 1/1 (molar ratio).

^b Ethylene and 4-phenyl-1-butene copolymers.

^c Ethylene and allylbenzene copolymers.

^d [AlCl₃]/[aromatic nuclei] (molar ratio).

^e Results from ¹H NMR analysis, given per 100 carbon atoms in the copolymer backbone.

^f Weight-average molecular weight and polydispersity index determined by GPC.

^g Melting temperature determined by DSC.

3. Results and discussion

3.1. Synthesis of functional polyolefins

For the sake of overcoming the shortcoming that the polar comonomers significantly reduce catalyst activity in direct insertion-type copolymerization, we chose allylbenzene and 4-phenyl-1-butene as reactive comonomers which are free of catalyst-deactivating heteroatoms but facile in functional transformation reactions. When the copolymers as reactive “intermediate” were prepared by the copolymerization of ethylene with allylbenzene or 4-phenyl-1-butene, the pendent phenyls of them can serve as reactive sites to bring carboxylic acid as strong polar groups into the polymer chains by F–C acylation reactions.

F–C acylation reactions are aromatic substitution reactions in which benzene (or substituted benzene) undergoes acylation when treated with carboxylic acid derivatives (usually acyl halide or anhydride) and a Lewis acid catalyst, such as AlCl₃ [17]. They have often been used as the initial reaction in a number of methods for the preparation of functionalized polystyrenes because they are mild and easily operated, and no toxic problems are involved, as well. However, there is only limited information about acylation of ethylene rich copolymers because it is not convenient to introduce phenyl groups into polyethylene. The F–C acylation reactions are applied to polystyrene widely. However, the crosslinking reaction of acylated macromolecules usually occurs in F–C acylation process of polystyrene, which leads to changes in the molecular mass and the solubility of the modified polymers. In order to overcome these problems, Hird and Eisenberg reported a simple method that aluminum chloride and acetyl chloride are allowed to react together prior to addition to the substrate for the preparation of partial *p*-carboxylation of linear polystyrene

without degradation or crosslinking [16b]. However, when we try the way, we only obtained ethylene rich copolymer with very low acylation rate. It is well established that the ratio of catalyst to acyl component and the sequence in which the reactants are mixed can be of great importance in F–C acylation reactions. So we try to challenge the subject by changing the reaction conditions and sequence to get high acylation rate copolymer without degradation or crosslinking.

In this study, there are few residual double bonds in the ethylene and allylbenzene/4-phenyl-1-butene copolymers, so to great extent that it avoids the crosslinking in acylation reaction. The ordinary acylation solvents could be carbon disulfide, nitrobenzene, dichloromethane and tetrachloroethane. The two copolymers can dissolve in high-boiling chlorinated solvents and nitrobenzene only at elevated temperature, but we cannot obtain satisfying results. Thus, we chose carbon disulfide as acylation solvent, which can dissolve the copolymer sufficiently at lower temperature and also be a good carrier for F–C catalyst. The other factor that controls the nature of acylated copolymer is the sequence in which the reactants are mixed. It is noteworthy that if the anhydrides were added at the primary stage, it would lead to crosslinking, furthermore the gelatin also occurred if the anhydrides were added fast at the last stage. In order to obtain the copolymers without crosslinking, we must add the anhydrides in batches and slowly. Other parameters such as the amount of AlCl₃, reaction temperature and reaction time were also examined so as to optimize the process. The degree of acylation corresponding to carboxylic acid value of the copolymers and the residual pendant aromatic groups was determined by ¹H NMR and the data are presented in Table 1.

When acylating the ethylene and 4-phenyl-1-butene copolymers, there is a considerable shedding of phenyls with the increase of temperature. At the same time, the rate of acylation

increases and the melting temperature (T_m) also increases somewhat. This can be explained by considering that the F–C alkylation and F–C acylation have similar reaction conditions. So as the F–C acylation happens, the F–C alkylation can also take place. However, the F–C alkylation is sufficiently reversible, which ultimately leads to the thermodynamically most stable product by alkylation–dealkylation. As for ethylene and 4-phenyl-1-butene copolymers, there is larger steric bulk between the benzene rings and the copolymer backbone, so the dealkylation will happen more easily. The considerable shedding of benzene rings heightens the extent of crystallization of the copolymer, which causes the increase of T_m . In order to obtain acylated copolymer without cross-linking and degradation, we select ethylene and allylbenzene copolymers to investigate further.

As show in Table 1, when the temperature was raised from 10 to 50 °C (entries 6–8), the amount of carboxyl groups increased noticeably, while the phenyls' pendant on the polymer backbone only slightly diminished. As well, the molar ratio of $[AlCl_3]/[GA]$ plays an important role on the degree of acylation in the F–C acylation reactions. As the ratio of $[AlCl_3]/[GA]$ was systematically varied from 2:1 to 6:1 (entries 8–10 in Table 1), the carboxyl groups also increased significantly, meanwhile the benzene ring content did not really change obviously. To further investigate the effect of reaction time on the degree of acylation, we prolonged the reaction time to 2 h and found that almost all the residual benzene rings acylated at the cost of slight brushing aromatic nuclei off. In the optimal reaction conditions, we conducted the similar acylation reactions with SA and PA, and got resemblant trend. When using PA as acylating agent, the degree of acylation is more sensitive to reaction time than GA and SA. One plausible explanation for the observed result is that the steric bulk of PA affects the access to aromatic nuclei, so accomplishing acylation reaction needs more reaction time for PA. All the acylated copolymers are soluble and sufficiently characterized.

3.2. Characterization of functional polymers

FT-IR was the first spectroscopic tool we used to identify our successful acylation of the ethylene and allylbenzene copolymers. The FT-IR spectra of the pristine copolymer and the acylated copolymers with GA, SA and PA in the range 3500–600 cm^{-1} are given in Fig. 1a–d, respectively, corresponding to the product coming from entries 5, 11, 13 and 15 in Table 1. By comparing the above four spectra, it is clear that in the spectra of the acylated copolymers (traces b, c and d) new peaks, which are absent in the spectrum of the pristine copolymer (trace a), can be ascertained. The new peaks at 1684 and 1708 cm^{-1} in Fig. 1b are ascribable, respectively, to different carbonyl functional groups of individual ketone and acid carbonyl groups. The new peaks at 1685 and 1711 cm^{-1} in Fig. 1c are similarly ascribable, respectively, to individual ketone and acid carbonyl groups. The new peaks at 1674 and 1695 cm^{-1} in Fig. 1d can be assigned to the diaryl ketone and isolated aromatic carboxylic acid carbonyl groups,

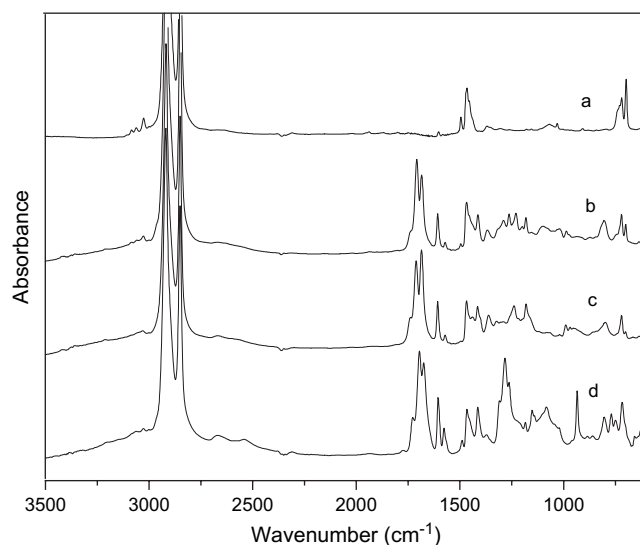


Fig. 1. FT-IR spectra of pristine copolymer (a) and the acylated copolymers with GA (b), SA (c) and PA (d) in the range 3500–600 cm^{-1} .

respectively. When carbonyl groups conjugate with more aromatic groups, the wavenumber of carbonyl groups will be lower.

1H NMR and two-dimensional 1H – 1H COSY spectral analyses unambiguously reveal the microstructure of the acylated copolymers. Because of the homogeneity of the reaction, the distribution of the acylate groups is believed to be random along the polymer chains. Fig. 2 shows the 1H NMR spectra of starting copolymer (A) and acylated copolymers with SA (B), GA (C) and PA (D). Fig. 2A displays typical 1H NMR spectrum of the starting copolymer with five peaks (δ 1.25, 1.60, 2.51, 7.11 and 7.22 ppm). When acylation with SA, two new characteristic signals (δ 2.74 and 3.23 ppm) were observed for the methylene protons of $-COCH_2CH_2COOH$ moiety, corresponding to the product coming from entry 12 in Table 1. Also when acylation reaction with GA, three new characteristic signals (δ 2.05, 2.46 and 3.00 ppm) were observed for the methylene protons of $-COCH_2CH_2CH_2COOH$ moiety, corresponding to the product coming from entry 8 in Table 1. When acylation with PA, four new characteristic signals (δ 7.33, 7.52, 7.57 and 8.01 ppm) were detected for dicarbonyl aromatic protons, corresponding to the product coming from entry 14 in Table 1. These new peaks sufficiently prove that the pendant benzene rings have been acylated.

To further reveal the slight influence of the acylation reaction upon the chemical shifts of starting copolymer, 1H – 1H COSY was performed as shown in Figs. 3 and 4, corresponding to Fig. 2C and D, respectively. All the peaks of acylated copolymers can be accurately attributed. It is noteworthy that the acylation reaction by anhydrides occurred exclusively at the *para*-position with respect to the substituent of the aromatic ring. It is rational because acylation is an electrophilic reaction, and there is no enough steric bulk to insert the complexes of anhydrides and $AlCl_3$ between the copolymer backbone and the *ortho*-position of phenyls. The chemical shifts of all the peaks are shown in Fig. 5.

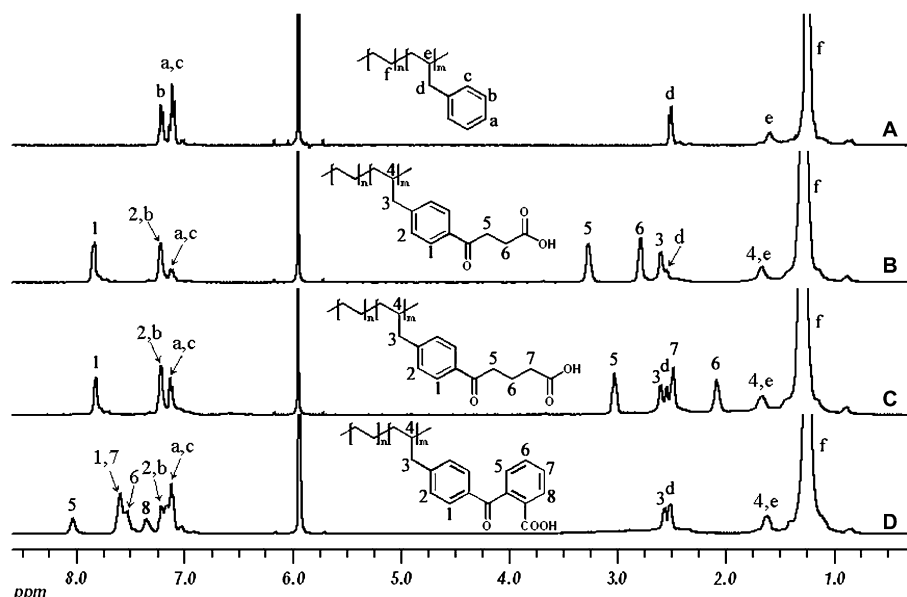


Fig. 2. ¹H NMR spectra of pristine copolymer (A) and the acylated copolymers with SA (B), GA (C) and PA (D).

The amount of phenyls in starting copolymers (N_s) and acylated copolymers (N_a) can be calculated by Eqs. (1) and (2).

$$N_s = [(I_d/2)/(I_f/2 + I_e) \times 100] \quad (1)$$

$$N_a = \{[(I_d + I_3)/2]/[I_f/2 + (I_e + I_4)]\} \times 100 \quad (2)$$

Here, the symbol I represents the resonance integrals and the subscripted numbers refer to the peak numbers, as shown in Fig. 2. N_s and N_a refer to the total number of pendant aromatic groups given per 100 carbon atoms in the backbone. It should be noted that the aromatic nuclei pendant on the backbone

only slightly diminish, so we can conclude that neither cross-linking nor degradation occurs to a significant extent during the acylation reaction of the copolymer.

The amount of carboxyl groups of acylated copolymers with GA (N_{GA}), SA (N_{SA}) and PA (N_{PA}), respectively, can be estimated from the relative intensities of the respective signals in ¹H NMR spectra according to the following Eqs. (3)–(5):

$$N_{SA} = \{[(I_5 + I_6)/4]/[I_f/2 + (I_e + I_4)]\} \times 100 \quad (3)$$

$$N_{GA} = \{[(I_5 + I_6)/4]/[I_f/2 + (I_e + I_4)]\} \times 100 \quad (4)$$

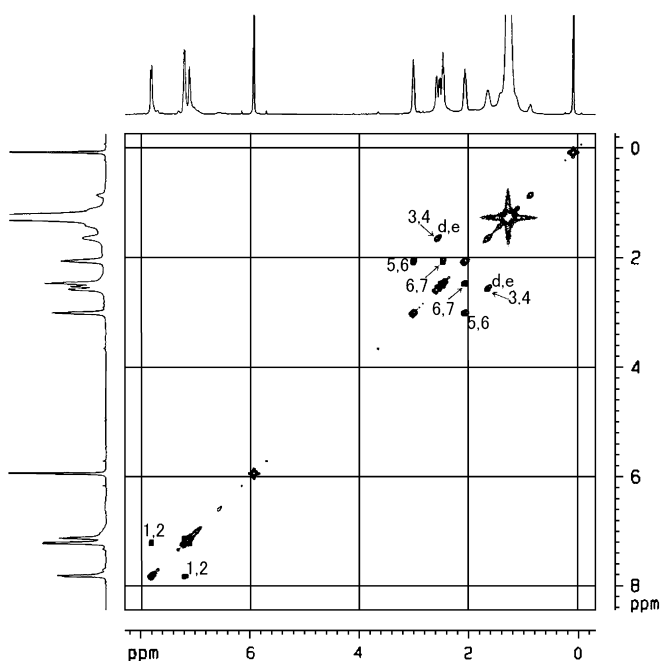


Fig. 3. ¹H–¹H COSY spectrum of acylated copolymer with GA.

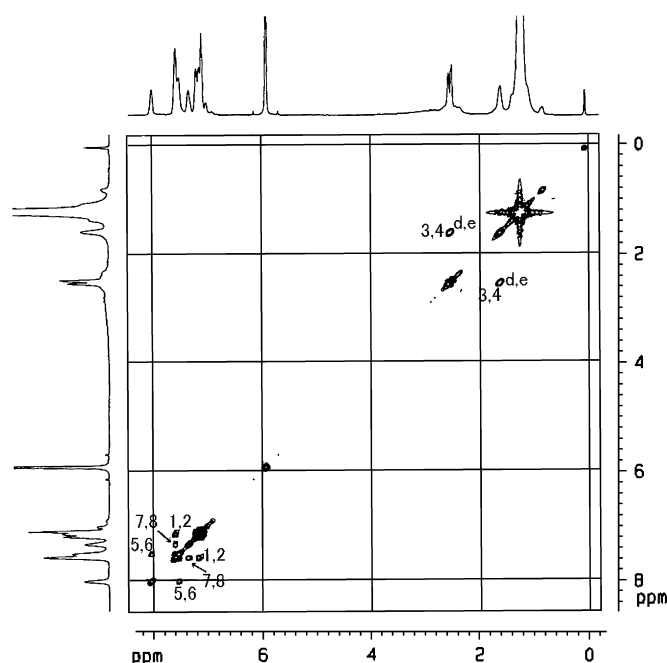


Fig. 4. ¹H–¹H COSY spectrum of acylated copolymer with PA.

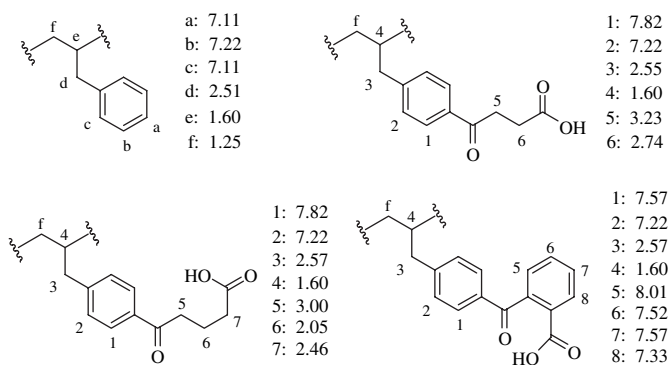


Fig. 5. ^1H data for acylated copolymers.

$$N_{\text{PA}} = \left\{ I_5 / [I_f/2 + (I_e + I_4)] \right\} \times 100 \quad (5)$$

where N_{SA} , N_{GA} and N_{PA} refer to the total number of pendant carboxyl groups given per 100 carbon atoms in the backbone. By comparing the data of N_{SA} , N_{GA} , N_{PA} and N_a , the most interesting feature we observe is that almost all the aromatic groups (more than 90%) are acylated with any anhydride in the optimum reaction conditions. Overall, the F–C acylation is very effective to introduce carboxylic acid units into the starting nonpolar copolymer.

GPC results show that the molecular weight of the acylated copolymer with GA decreases somewhat with the increasing degree of acylation (entries 5–11 in Table 1). The similar results were obtained when we use SA (entries 12 and 13 in Table 1) and PA (entries 14 and 15 in Table 1) instead of GA. This was not expected because the incorporation of the carboxylic acid groups should have increased the molecular weight of the ethylene and allylbenzene copolymers. The somewhat decrease in molecular weight may indicate that some acylated copolymer conglomerate is more compact than the parent copolymer molecule due to the formation of hydrophilic domains. A similar result was observed for the published sulfonation polymer [18]. More importantly, one can conclude that neither crosslinking nor degradation occurred to a significant extent during the acylation reaction of the copolymer because the $\overline{M}_w/\overline{M}_n$ of acylated copolymers did not increase.

DSC results show that the T_m s of acylated copolymers with GA decrease slowly as the amount of carboxylic acid groups is raised from 0 to 1.54 (entries 5–7 and 9 in Table 1) but then increase significantly as the degree of acylation is raised further. The phenomenon can be explained as follows: when a small quantity of noncrystallizable comonomer units is randomly incorporated into the backbone of a crystallizable polymer, the degree of crystallinity of the polymer will decrease. Therefore, the melting temperature also decreases. However, with the degree of acylation increasing further, the interactions among the acid groups, e.g. hydrogen bonding, become the main factor affecting the T_m . Thus, the T_m of acylated copolymer increases obviously as the carboxylic groups in the copolymer reach some degree. The acylated copolymers with SA have the similar trend, however, when the acylating agent is PA, there is no obvious effect on T_m with the degree of

acylation increasing due to the large size of the aromatic group linking carboxyl group which hinders the interactions among the acid groups.

4. Conclusions

Carboxyls as strong polar groups were introduced effectively into nonpolar ethylene and allylbenzene copolymers without obvious degradation or crosslinking by convenient F–C acylation reaction, avoiding the shortcomings of direct insertion-type copolymerization of ethylene and polar comonomers. FT-IR, ^1H NMR and ^1H – ^1H COSY spectroscopic analyses unambiguously reveal the microstructure of the acylated copolymers. NMR has been shown to be, once again, a very powerful tool and the only technique that permits elucidation of, with some accuracy, the polymer microstructure study. The functionalized polyolefin offers possibility for the development of novel ethylene rich copolymer blends and composites, thus extending the application field of nonpolar polyolefin.

Acknowledgements

The authors are grateful for subsidy provided by the National Natural Science Foundation of China (nos. 20334030 and 50525312) and by the National Basic Research Program of China (no. 2005CB623800).

References

- [1] For reviews of functionalized polyolefins, see:
 - (a) Padwa AR. *Prog Polym Sci* 1989;14:811–33;
 - (b) Dong JY, Hu YL. *Coord Chem Rev* 2006;250:47–65;
 - (c) Boaeen NK, Hillmyer MA. *Chem Soc Rev* 2005;34:267–75.
- [2] Boffa LS, Novak BM. *Chem Rev* 2002;100:1479–93.
- [3] (a) Mecking S, Johnson LK, Wang L, Brookhart M. *J Am Chem Soc* 1998;120:888–99;
 - (b) Heinemann J, Mühaupt R, Brinkmann P, Luinstra G. *Macromol Chem Phys* 1999;200:384–9;
 - (c) Meneghetti SP, Kress J, Lutz PJ. *Macromol Chem Phys* 2000;201:1823–32;
 - (d) Boone HW, Athey PA, Mullins MJ, Philipp D, Muller R, Goddard WA. *J Am Chem Soc* 2002;124:8790–1;
 - (e) Britovsek GJP, Gibson VC, Spitzmesser SK, Tellmann KP, White AJP, Williams DJ. *J Chem Soc Dalton Trans* 2002;1159–71;
 - (f) Liu JY, Zheng Y, Li YS. *Polymer* 2004;45:2297–301.
- [4] (a) Chung TC, Rhubright D. *J Polym Sci Part A Polym Chem* 1993;31:2759–63;
 - (b) Marathe S, Sivaram S. *Macromolecules* 1994;27:1083–6;
 - (c) Lipponen S, Seppala J. *J Polym Sci Part A Polym Chem* 2004;42:1461–7;
 - (d) Chung TC, Rhubright D. *Macromolecules* 1993;26:3019–25;
 - (e) Cao CG, Zou JF, Dong JY, Hu YL, Chung TC. *J Polym Sci Part A Polym Chem* 2005;43:429–37;
 - (f) Nam YG, Shiono T, Ikeda T. *Macromolecules* 2002;35:6760–2;
 - (g) Dong JY, Hong H, Chung TC. *Macromolecules* 2003;36:6000–9;
 - (h) Chung TC, Dong JY. *Macromolecules* 2002;35:2868–70;
 - (i) Fan GQ, Dong JY, Wang ZQ, Chung TC. *J Polym Sci Part A Polym Chem* 2006;44:429–37;
 - (j) Zhang YC, Chen JY, Li HL. *Polymer* 2006;47:4750–9.

- [5] (a) Wang L, Meng YZ, Wang SJ, Li XH, Xiao M. *J Polym Sci Part A Polym Chem* 2005;43:6411–8;
(b) Yang JE, Lee JS. *Electrochim Acta* 2004;50:617–20;
(c) Jang BB, Lee K, Kwon WJ, Suh J. *J Polym Sci Part A Polym Chem* 1999;37:3169–77;
(d) Roscoe SB, Gong CG, Fréchet JMJ, Walzer JF. *J Polym Sci Part A Polym Chem* 2000;38:2979–92;
(e) Fernyhough CM, Young RN, Ryan AJ, Hutchings LR. *Polymer* 2006;47:3455–63.
- [6] (a) Hou ZM, Luo YJ, Li XF. *J Organomet Chem* 2006;691:3114–21;
(b) Lahitte JF, Plentz-Meneghetti S, Peruch F, Muller R, Lutz PJ. *Polymer* 2006;47:1063–72;
(c) Craymer JF, Kas RM, Coughlin EB. *Polyhedron* 2005;24:1347–55;
(d) Ishiyama T, Miyoshi K, Nakazawa H. *J Mol Catal A Chem* 2004;221:41–5;
(e) Gentil S, Pirio N, Meunier P, Gallou F, Paquette LA. *Eur Polym J* 2004;40:2241–6.
- [7] (a) Lu B, Chung TC. *J Polym Sci Part A Polym Chem* 2000;38:1337–43;
(b) Sangeetha D. *Eur Polym J* 2005;41:2644–52;
(c) Shim SY, Weiss RA. *Polym Int* 2005;54:1220–3;
(d) Zhang GI, Liu L, Wang HM, Jiang M. *Eur Polym J* 2000;36:61–8;
(e) Zou JF, Cao CG, Dong JY, Hu YL, Chung TC. *Macromol Rapid Commun* 2004;25:1797–804;
(f) Dong JY, Manias E, Chung TC. *Macromolecules* 2002;35:3439–47.
- [8] (a) Dong JY, Chung TC. *Macromolecules* 2002;35:1622–31;
(b) Chung TC, Dong JY. *J Am Chem Soc* 2001;123:4871–6;
(c) Dong JY, Wang ZM, Hong H, Chung TC. *Macromolecules* 2002;35:9352–9;
(d) Kandil U, Chung TC. *J Polym Sci Part A Polym Chem* 2005;43:1858–72;
(e) Liu YY, Hu YL, Mike Chung TC. *Polymer* 2005;46:10585–91.
- [9] (a) Byun DJ, Shin DK, Kim Y. *Macromol Rapid Commun* 1999;20:419–22;
(b) Kumar KR, Sivaram S. *Polym Int* 2001;50:367–74;
(c) Byun DJ, Choi KY, Kim SY. *Macromol Chem Phys* 2001;202:992–7.
- [10] (a) Reybuck S, Waymouth RM. *J Polym Sci Part A Polym Chem* 2004;42:3323–31;
(b) Byun DJ, Kim SY. *Macromolecules* 2000;33:1921–3;
(c) Tang LM, Hu T, Pan L, Li YS. *J Polym Sci Part A Polym Chem* 2005;43:6323–30;
(d) Naga N, Toyota A. *Polymer* 2004;45:7513–7;
(e) Paaola S, Saarinen T, Löfgren B, Pitänen P. *Polymer* 2004;45:2099–110;
(f) Pan L, Liu YG, Zhang KY, Bo SQ, Li YS. *Polymer* 2006;47:1465–72;
(g) De Rosa C, Auriemma F. *Polymer* 2006;47:2179–88;
(h) Uotila R, Hippo U, Paaola S, Seppälä J. *Polymer* 2005;46:7923–30;
(i) Grisi F, Pragliola S, Costabile C, Longo P. *Polymer* 2006;47:1930–4.
- [11] (a) Hakala K, Helaja T, Löfgren B. *J Polym Sci Part A Polym Chem* 2000;38:1966–71;
(b) Lehmus P, Kokko E, Härkki O, Leino R, Luttikhedde HJG, Näsman JH, et al. *Macromolecules* 1999;32:3547–52;
(c) Britto ML, Galland GB, dos Santos JHZ, Forte MC. *Polymer* 2001;42:6355–61.
- [12] (a) Xu H, Hu XZ. *J Polym Sci Part A Polym Chem* 1998;36:2151–4;
(b) Tabak G, Pham TN, Levesque G, Haraoubia R. *J Polym Sci Part A Polym Chem* 1998;36:117–27.
- [13] Cheng SK, Wang CC, Chen CY. *Mater Chem Phys* 2003;78:581–90.
- [14] (a) Pesonen H, Sillanpää A, Aksela R, Laasonen K. *Polymer* 2005;46:12641–52;
(b) Pesonen H, Sillanpää A, Aksela R, Laasonen K. *Polymer* 2005;46:12653–61;
(c) Zhang GZ, Jiang M, Zhu L, Wu C. *Polymer* 2001;42:151–9.
- [15] (a) Bazunova MV, Kolesov SV, Korsakov AV. *Russ J Appl Chem+* 2006;79:853–5;
(b) Combellas C, Fuchs A, Kanoufi F, Mazouzi D, Nunige S. *Polymer* 2004;45:4669–75;
(c) Polyakova IV, Pisarev OA. *J Chromatogr A* 2005;1092:135–41.
- [16] (a) Liu L, Jiang M. *Macromolecules* 1995;28:8702–4;
(b) Hird B, Eisenberg A. *J Polym Sci Part A Polym Chem* 1993;31:1377–81.
- [17] Andrew SJ. *Introduction to organic chemistry*. New York: Wiley; 1971.
- [18] Wang SH, Zeng ZH, Yang SH, Weng LT, Wong PCL, Ho K. *Macromolecules* 2000;33:3232–6.