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Synthesis of graft copolymer of styrene and acrylonitrile onto poly (butyl acrylate) by using polymeric peroxide

Xuezhen Shi[1], Weizhuang Cheng[1] (✉), Zhixiang Lu[2], Qiangguo Du [2] (✉), Yuliang Yang[2]

[1] School of Materials, Tongji University, Shanghai 200092, People's Republic of China

[2] Department of Macromolecular Science, Fudan University, the Key Laboratory of Molecular Engineering of Polymers, Shanghai 200433, People's Republic of China

email: qgdu@fudan.edu.cn, Tel.: +86-21-65643891, Fax: +86-21-65640293

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Summary

Two-stage seeded emulsion copolymerization of butyl acrylate with tert-butyl 3-isopropenylcumylperoxide (D120) was performed at 70°C . Copolymer latex with 0.2μm of particle size was obtained. Emulsion graft polymerization of styrene and acrylonitrile onto the copolymer of butyl acrylate was initiated by peroxy bonds in the D120 units of the backbone chains at 120°C . Graft copolymers with higher grafting ratio were derived. It was found that the grafting ratio tends to increase with the increasing D120 in feed of copolymerization with butyl acrylate. The graft copolymers were blended with SAN resin, and a kind of AAS resin was obtained. Both elongation at break and Izod impact strength of the AAS resin reached maximum at grafting ratio of 0.25, which were comparable with the values of ABS resin for general purpose. A method to improve the grafting efficiency on the saturated polyacrylate elastomer rubber was developed.

Introduction

Graft copolymers are required widely in various application fields of polymer alloys (blends), compatibility improvements, surface modifications, and so on. The processes to prepare graft copolymers has been investigated intensively including radical graft copolymerization, which can be performed by using special initiators, chain transfer reaction [1], radiation polymerization [2,3], light polymerization[4], and mechanics [5,6]. Recently studies on controlled radical copolymerization, especially the atom transfer radical polymerization (ATRP), were developed for preparation of graft copolymer [7-11], by which the graft copolymers of well-controlled molecular weight and molecular weight distribution can be obtained. On the other hand, polymeric peroxides have also been studied with regard to their potential initiating characteristics in vinyl polymerization to prepare block and graft copolymers [12-14]. Graft copolymers initiated by the thermal cleavage of pendant proxy bonds always result in higher grafting efficiency [13].

ABS resin is a widely used plastic; however, the polybutadiene in the resin is easy to be oxidized. The use of saturated rubber instead of polybutadiene has been tried to overcome the poor weatherability of ABS resin. Usually it is difficult to graft onto the saturated rubber because of its chemical stability.

The purpose of this paper is to develop a process to improve the grafting efficiency on the poly (butyl acrylate), which is saturated and mostly used as rubber backbone in AAS resin. First, the copolymerization of butyl acrylate (BA) with tert-butyl 3-isopropenylcumylperoxide (D120), a commercially available polymeric peroxide, was performed in emulsion. Next, the graft of styrene (St) and acrylonitrile (AN) onto the copolymer of BA/D120 initiated by the pendant peroxy bonds was studied. In addition, the relationship between grafting ratio and mechanical properties of the AAS resin thus obtained was studied as well.

Experimental

Materials

Styrene (St), butyl acrylate (BA), and acrylonitrile (AN) from Shanghai Gaoqiao petrochemical Co. and ethylene glycol dimethacrylate (EGDM) from Tokyo Kasei Kogyo Co were purified by distillation under reduced pressure before use. D120 was kindly supplied by Kayaku AKZO Co (Japan). The oligomer and other impurities in D120 were removed by precipitation in methanol, which was removed then by distillation under reduced pressure. Potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) from reputable suppliers were used as received. Sodium dimethyl dithiocarbamate was obtained from Shanghai Changjiang Chemical Co., and water solution of 10wt% was prepared for use. SAN resin (24wt% of AN content, 2.2 g/10min of Melt Index) was purchased from Lanzhou Petrochemical Co., and dried in oven at 60°C for 5h before use.

Preparation of copolymer of BA with D120

Two-stage seeded emulsion copolymerization was performed to prepare the copolymer latex with 0.2 μm of particle size. At first 100g of BA was added to 250g of water containing 1.2g of SDS and 0.3g of KPS, the mixture was stirred under nitrogen for 4h at 70°C . Latex with 0.085μm of particle size was obtained and used as seed. In the second stage monomer mixture consisting of 97.5g of BA, D120 and 1g of EGDM was added dropwise to 100g of water containing 0.1 g of KPS and 2.5g (by solid) of seed latex within 4h at 70°C with stirring and under nitrogen. At the same time additional 0.2g of KPS and 1g of SDS were dissolved in 25g water and added in batches. After addition was complete, stirring was continued for another 2h at 70°C . The conversion, usually higher than 95% °C was calculated from total solid content.

Characterization of the copolymer latex

Particle size and particle size distribution of latex was measured on BECKMAN COULTER LS230 Particle Size Analyzer.

Some latex of the copolymer was precipitated, filtered, washed extensively with water, and soaked in excessive methanol for 24 hr to remove residual monomer, then dried in vacuum below 50°C . The solid product obtained was used for gel determination, Raman analysis and DSC measurement.

0.5 g samples obtained above (accurately weighed) were added to the tubes containing 50ml toluene and kept swelling at room temperature for 96 h. After filtration with metal mesh and drying under vacuum, the gel percentage was calculated. The degree of swelling Q was calculated as follows:

$$Q= (W_1/\rho_1+ W_2/\rho_2)/ (W_2/\rho_2)$$

Where W_1 and W_2 are the weight of solvent and copolymer in the swollen gels respectively, and ρ_1 and ρ_2 are the density of solvent and copolymers before swelling. All the results are listed in Table 1.

Differential Scanning Calorimetry (DSC) analysis was performed on a Natzsch DSC-200 instrument, with the heating rate of 10°C /min, while nitrogen gas purge was used.

Raman Spectra were recorded with a LabRam-1B Micro-spectrometer, with excitation line of 631.81nm and power of 6mw.

Synthesis of graft copolymer

A 200ml autoclave was charged with 100g of water, 22g of St, 8g of AN, 0.4g of SDS, 0.4ml of aqueous solution of sodium dimethyl dithiocarbamate, and 20g of copolymer latex (by solid) obtained above. Solution of sodium dimethyl dithiocarbamate was used as a terminator to react with the residual KPS, which may initiate homopolymerization or copolymerization of St and AN and decrease grafting efficiency. After purged by nitrogen, the autoclave was sealed and stirred, then heated to 120°C gradually within 2h and kept for another 4h. After coagulation, filtration, washing and drying in vacuum, the powder product of graft copolymer was obtained.

Determination of grafting ratio

0.5g of dried powder product obtained above was immersed in 50ml of acetone for 48h at room temperature. The insoluble residue, composed of graft copolymer and ungrafted poly (butyl acrylate), was separated from solution, which containing binary copolymer of St and AN, on ultracentrifuge, and washed with acetone for three times. The grafting ratio was calculated from IR spectrum, which was recorded on a Nicolet Magna 550 FTIR spectrometer. Calibration curve for IR analysis was established by using a series of quantitatively prepared blends of poly (butyl acrylate) and SAN (copolymer of St and AN) in various compositions. The peak heights of absorption at $2237cm^{-1}$, $1735cm^{-1}$ and $701cm^{-1}$, assigned to monomer units of AN, butyl acrylate and St in graft copolymer respectively, was measured.

Blending and mechanical properties testing

The graft copolymer obtained above was blended with SAN resin in a Brabender mixer with a capacity of 60g at 220°C for 5min, with rotor speed of 45 rpm. In every blend sample the content of poly (butyl acrylate) was kept as 20(wt) %. Standard bar was prepared by compression molding at 200°C . Tensile properties and notched Izod impact strength were measured according to ASTM D638 and ASTM D256, respectively. Five to ten bars were tested on each instrument and standard deviation of less than 20% was found for each property.

Morphology observation

Morphology of undeformed molded test specimens was examined using a Hitachi H-600 TEM. The sample was stained with Ruthenium solution for 10 days, and then cut on a Riechet-Jung Ultramicrotome.

Results and discussion

Copolymer latex

Main features of the BA/D120 copolymer latex, such as conversion, gel percentage, swelling degree in toluene and particle size, are summarized in Table1. Generally, in the preparation of ABS resin the important aspects of the rubber substrate affecting properties such as impact, flow, and surface gloss are the average rubber particle size and particle size distribution. Larger than 0.2μm of diameter is believed to be required for satisfying high impact value. As shown in Table1, after two-stage seeded emulsion polymerization, the particle sizes of the copolymer latex were about 0.2μm in diameter, which can meet the requirement for toughening purpose in SAN matrix. On the other hand in the rubber-toughened resin cross linking of the rubber component is also required to some extent to minimize deformation of the rubber particles. Table1 shows that EGDM, as a diene-type monomer, is effective in cross linking the rubbery product, gel fraction of which was 80% or more.

The existence of D120 monomer units in the copolymer molecules was confirmed by both Raman spectra and DSC curves. The content of D120 introduced to the copolymer in the present research was so trifle that the feature absorption peaks of D120 units on the normal IR spectra were too weak to be distinguished. Therefore, the more sensitive Raman spectrometer was used. Figure 1 shows the Raman spectra of copolymer D120 (3wt %) with BA and homopolymer of BA. In comparison to homopolymer of BA, the copolymer has absorption at 1006cm^{-1} assigned to meta-substituted benzene ring, which was introduced by incorporating D120. The result indicates that the copolymerization of D120 with BA took place, which was also confirmed by DSC measurements. As shown in Figure 2, an exothermic peak corresponding to the characteristic decomposition of peroxy groups in D120 [15] emerges around 190°C on the DSC curves of the product of copolymerization. The area of the exothermic peak increases gradually with increasing of D120 in feed whereas the product in the absence of D120 in feed shows no exothermic peak there. Accordingly, the result shows that the units of D120 have been incorporated to polymer chains, and the pendant O-O bonds of D120 units survived after copolymerization at 70°C . The product is real copolymer of butyl acrylate with D120.

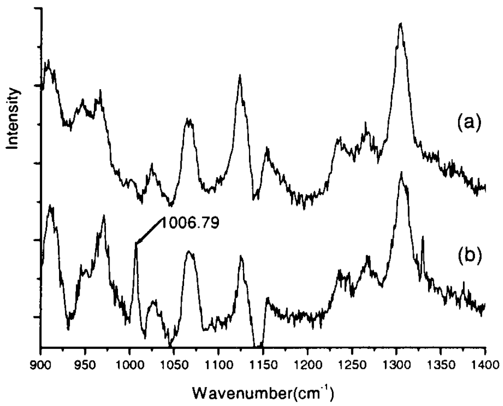


Figure 1. Raman spectra of homopolymer of BA (a) and copolymer of BA and D120(3wt%) (b)

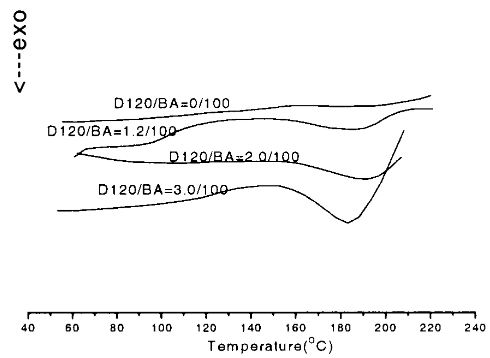


Figure 2. DSC curves of the copolymers of BA and D120 with various D120 content in feed

Table 1. Characteristics of copolymers latexes of BA with D120

BA/D120 (Wt)	Conversion (%)	particle size in diameter(μm)	Gel percentage (%)	Swelling deg
100/0	99.0	0.210	80.9	20.6
100/0.4	99.9	0.218	85.4	19.3
100/0.8	97.0	0.225	86.1	18.1
100/1.2	99.9	0.218	87.0	18.8
100/1.6	95.8	0.216	81.8	21.7
100/2.0	96.2	0.194	82.6	26.9
100/3.0	99.1	0.212	83.1	42.8

Grafting ratio

The measurement result of grafting ratio, which is defined as the weight ratio of grafted SAN to the backbone of the copolymer of butyl acrylate, is shown in Figure 3. The grafting ratio tends to increase with the increasing D120 in feed of copolymerization with butyl acrylate. The result means that the more D120 units introduced to the backbone, the more graft sites created by decomposition of the pendant peroxy bonds on the backbone during graft polymerization at 120°C .On the other hand, graft copolymerization of St and AN onto the copolymer of BA with D120 may also take place via chain transfer, which resulted in a finite grafting ratio for zero D120/BA% in feed.

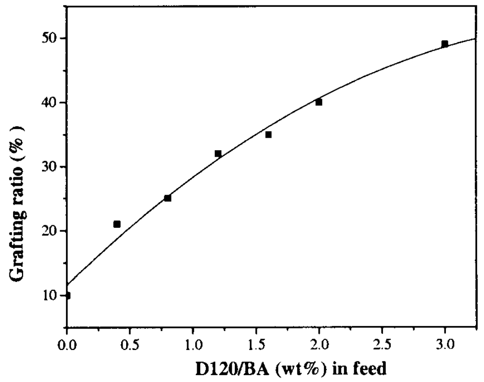
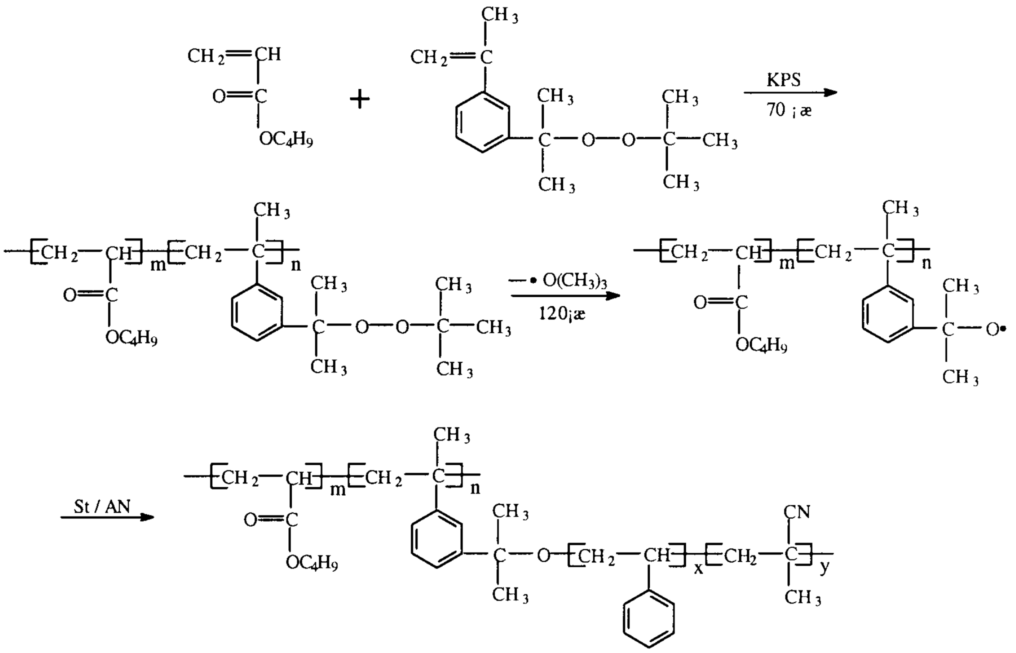


Figure 3. The effect of D120 content in feed on grafting ratio

It can be found that a certain amount of SAN was not grafted onto the backbone. It may be attributed to the copolymerization of AN with St initiated by heat or by fragmentary free radicals produced during decomposition of pendant peroxy bonds on the backbone.

The copolymerization of butyl acrylate with D120 and the graft copolymerization of AN and St onto the copolymer can be shown schematically as follows:



Effect of graft ratio on the mechanical properties

The yield tensile strengths, elongation at breaks, and notched Izod impact strengths of blends of SAN with the product of graft copolymerization are shown in Figure 3. It can be seen that both elongation at break and Izod impact strength reached maximum, when D120/BA in feed was 0.8/100 yielding grafting ratio of 0.25. The result obtained in this study agreed closely with the conclusion of M.Rink [16], who reported that in the toughening of ABS resin, the impact strength increased as grafting ratio increased

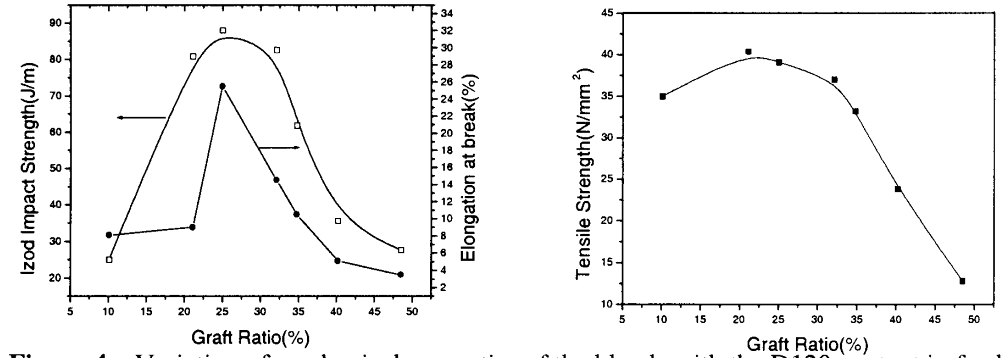


Figure 4. Variation of mechanical properties of the blends with the D120 content in feed of copolymerization with BA

and leveled off or decreased around 25% of grafting ratio due to the more presence of glassy subinclusion reducing the thermal stresses in the matrix surrounding the dispersed particles. Figure 4 also shows that the optimum mechanical properties of AAS obtained in this study are close to those of ABS resin.

Morphology

Although the weight fraction of Poly (butyl acrylate) in all the AAS samples was kept constant, photomicrograph obtained by TEM shows remarkable morphologic variations as the grafting ratio varies (Figure 5).

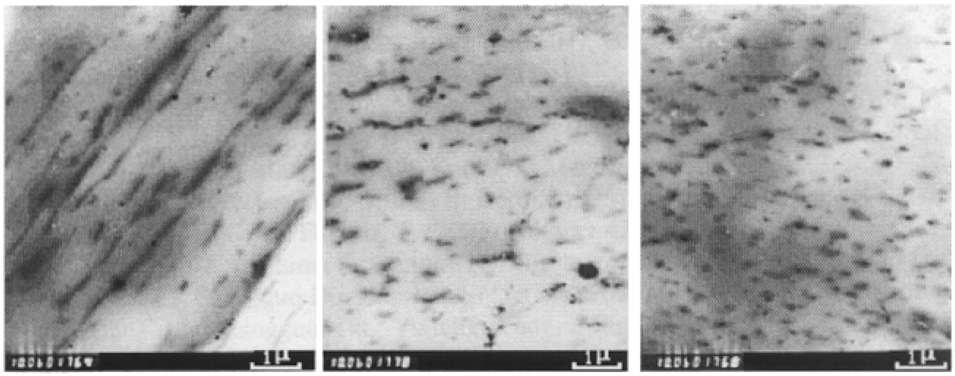


Figure 5. Transmission electron micrograph of undeformed AAS samples (stained by ruthenium) ,D120/BA in feed 0%(left),0.8%(middle),3.0%(right), and corresponding grafting ratio 10%,25%,49%

For scarcely grafted sample with grafting ratio of 10%, the incompatibility of poly (butyl acrylate) with matrix polymer induces the particle to coalesce, while for highly grafted sample with grafting ratio of 49%, the existence of an outer shell of SAN grafted on the rubber particles seems to prevent them from coalescing, so that rubber particles well dispersed in the matrix. The sample with intermediate grafting ratio of 25% showed “intermediate” dispersion of rubber particles with some clustering which is usually associated with improved impact strength in comparison to blends with uniform graft rubber particle dispersion [17].The electron micrograph indicates that many connected particles tends to line up in long rows likely due to the incomplete or wart-like graft coverage of the rubber particle. The similar morphology was observed by H.Keskkula [18].

Conclusions

The emulsion copolymerization of butyl acrylate with D120 was performed. Peroxy bonds of D120 units survived after reaction of copolymerization at 70°C . The free radicals produced during decomposition of the pendant peroxy bonds on the copolymer at 120°C can initiate the graft polymerization of AN and St onto the backbone of the copolymer. The grafting ratio tends to increase with increasing D120 in feed of copolymerization with butyl acrylate. Izod impact strength reached maximum when D120/BA in feed was 0.8/100 yielding grafting ratio of 0.25. A new method to raise grafting on the saturated polyacrylate rubber in the synthesis of AAS resin was developed.

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