Colloid Polym Sci (2002) 280: 835–840
DOI 10.1007/s00396-002-0691-2

W.S. Lyoo
H.W. Lee

Synthesis of high-molecular-weight poly(vinyl alcohol) with high yield by novel one-batch suspension polymerization of vinyl acetate and saponification

Received: 28 January 2001
Accepted: 4 March 2002

W.S. Lyoo (✉) · H.W. Lee
School of Textiles, Yeungnam University,
Kyongsan 712-749, Korea
E-mail: wslyoo@yu.ac.kr
Tel.: +82-53-8101126
Fax: +82-53-8123503

Abstract Generally, owing to tautomerism of vinyl alcohol monomer, poly(vinyl alcohol) (PVA) cannot be obtained by direct polymerization but it can be obtained by the saponification of poly(vinyl ester) precursors such as poly(vinyl acetate) (PVAc). In this study, to obtain high-molecular-weight (HMW) PVA with high yield through a one-batch method, we tried continuous saponification of PVAc prepared by suspension polymerization of vinyl acetate (VAc). We controlled various polymerization conditions, such as polymerization temperature, initiator concentration, suspending agent concentration, agitation speed, and VAc/water ratio, and obtained PVAc with a maximum conversion of VAc into PVAc of over 95–98%. PVA beads having various molecular parameters were prepared by continuous saponification of PVAc microspheres. Despite our employing a one-batch process, a maximum degree of saponification of 99.9% could be obtained. Continuous heterogeneous saponification of prepared PVAc yielded HMW PVA having a number-average degree of polymerization of 2,500–5,500, a syndiotactic diad content of 51–52%, and degree of saponification of 85.0–99.9%.

Keywords High-molecular-weight poly(vinyl alcohol) · One batch · Suspension polymerization · Maximum conversion · Continuous heterogeneous saponification

Introduction

Poly(vinyl alcohol) (PVA) cannot be prepared by direct polymerization owing to tautomerism of vinyl alcohol monomer [1, 2]. Thus, PVA is obtained by the saponification of a poly(vinyl ester), such as poly(vinyl acetate) (PVAc) or poly(vinyl pivalate) [3, 4, 5, 6, 7, 8, 9, 10, 11]. PVA fibers and films have high tensile and compressive strengths, a high tensile modulus, and good abrasion resistance owing to the large crystalline lattice modulus. To maximize these physical properties, the molecular weight, the degree of saponification (DS), and the syndiotacticity should be increased [3, 4, 5, 6, 7]. Especially, to increase the molecular weight, which is a fundamental factor affecting the physical properties, improvement of the polymerization methods of vinyl acetate (VAc) [12, 13, 14, 15, 16, 17] is necessary. Four polymerization methods of VAc (bulk, solution, emulsion, and suspension) are known [12, 13, 14, 15, 16, 17].

In the bulk polymerization of VAc, high-molecular-weight (HMW) PVAc and PVA can be obtained but it is very difficult to control the viscosity of the reaction mixture. Thus, HMW PVAc with high conversion is hardly obtained at the same time [10, 14, 16, 17]. To reduce the heat of polymerization and the viscosity of the medium, solution polymerization of VAc was tried. Although relatively higher conversion of VAc into PVAc is attained in the case of solution polymerization than bulk polymerization, it is nearly impossible to obtain HMW PVAc with a conversion of over 80% owing to the high viscosity of the reaction solution [11, 12]. It is known that the molecular weight and the polymerization rate increase simultaneously by emulsion polymerization of VAc. However, because side-chain formation reactions due to a higher propagation rate of VAc in the emulsion system result in branched HMW PVAc, it is nearly impossible to produce HMW PVA from PVAc by a saponification reaction [13, 15].

Commercially important polymers and copolymers were manufactured by suspension polymerization. The highest conversion can be achieved by suspension polymerization compared to other polymerization methods [17]. Suspension polymerization generally has been used for the production of polymer particles with diameters in the range 80–700 μm. The mechanism of suspension polymerization in a droplet is basically identical to that of bulk polymerization [18]. The water in the polymerization reaction solution reduces the exothermic heat and prevents viscosity enhancement during the polymerization [19, 20]. Owing to these advantages, suspension polymerization of VAc has the possibility to produce HMW PVAc with highest conversion which is a precursor of HMW PVA. Polymer particles produced in suspension polymerization have applications in chromatographic separations, biochemicals, bioengineering, drug-delivery systems, and they cancel cell-killing embolic materials [21, 22, 23].

Many researchers have been studying the suspension polymerization of VAc because it is possible to reach higher conversion than other polymerization methods [24, 25, 26]. Lyoo et al. [17] prepared HMW PVAc having a high yield at a polymerization temperature of 30 °C using a room-temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN). Murakami et al. [27] prepared microspheres of PVA with a diameter of about 10 μm by using a PVA–borate complex as a suspension agent. Cherng and Ping [22] prepared large, spherical PVA beads (up to 1.5-mm diameter) with a core-shell structure. As already described, in all industrial PVA preparation, a general two-batch process has been utilized. Studies on the one-batch suspension polymerization and saponification process are very rare because complete saponification of HMW PVAc with very high conversion is nearly impossible.

In this study, PVA was prepared by our novel one-batch process, which is very simple and an effective method of continuous saponification of HMW PVAc with high yield. The effects of the polymerization and saponification conditions on the number-average degree of polymerization (P_n), the degree of branching (DB), the DS, and the syndiotactic diad (s-diad) content of PVA prepared by a one-batch saponification and polymerization process were examined.

Experimental

Materials

VAc purchased from Shin-Etsu was washed with an aqueous solution of $NaHSO_3$ and with water, was dried over anhydrous $CaCl_2$, and was then distilled under a reduced pressure of nitrogen. The initiator ADMVN (Wako Co., 99%) was recrystallized twice from absolute methanol before use. PVA with a number-average molecular weight of 127,000 and a DS of 88% (Aldrich Co.) was used as a suspending agent. Other extra-pure-grade reagents were used without further purification. The water used for all the procedures was deionized.

One-batch preparation of PVA

Suspending agent (0.5 g) was dissolved in 100 ml water under a nitrogen atmosphere and constant stirring in a 250-ml reactor fitted with a condenser. VAc monomer (50 ml) along with the fixed amount of ADMVN after degassing were added simultaneously at a fixed polymerization temperature. The polymerization was conducted at a stirring rate of 500 rpm. Immediately after the polymerization, PVAc was saponified in aqueous $NaOH/Na_2SO_4/CH_3OH$ solution, and the saponification of PVAc was conducted for 2 days at 40, 50, and 60 °C. The $NaOH/Na_2SO_4/CH_3OH$ ratios in 100 ml water used in this study are 5/7.5/10, 10/7.5/10, and 15/7.5/10, respectively. The PVA prepared was filtered and washed with distilled water.

Acetylation of PVA

A mixture of 1 g PVA, 2 ml pyridine, 20 ml acetic anhydride, and 20 ml acetic acid was stirred in a three-necked flask at 100 °C for 24 h under an atmosphere of nitrogen. Then the mixture was poured into cold water to precipitate PVAc. The PVAc thus produced was filtered and purified by repeating the reprecipitation from methanol and water.

Characterization

The molecular weight of PVAc was calculated using Eq. (1):

$$[\eta]\ (\mathrm{dl/g}) = 8.91 \times 10^{-3} (P_n)^{0.62}\ (\text{in benzene at } 30^\circ\mathrm{C}), \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity and P_n is the number-average degree of polymerization of PVAc. The molecular weight of PVA was determined from that of PVAc produced by acetylation of PVA using Eq. (1).

The DB for the acetyl group of PVAc was calculated using Eq. (2) [2]:

$$\mathrm{DB} = (\mathrm{DP}_1/\mathrm{DP}_2) - 1, \qquad (2)$$

where DP_1 is P_n of PVAc and DP_2 is P_n of PVA prepared by saponifying PVAc.

The s-diad contents of PVA were determined using a ^1H NMR spectrometer (Varian, Sun Unity 300). The DS of PVA was determined by the weight loss after saponification and by the ratio of the methyl and methylene proton peaks in the ^1H NMR spectrum.

The crystal melting temperature (T_m) of PVA was measured using a differential scanning calorimeter (Perkin Elmer, DSC 7) with a sample weight of 10 mg and at a heating rate of 10 °C/min.

The surface morphologies of the PVA beads were examined with a scanning electron microscope (JSM 5800-LV, Jeol, Japan) with a magnification of 160×.

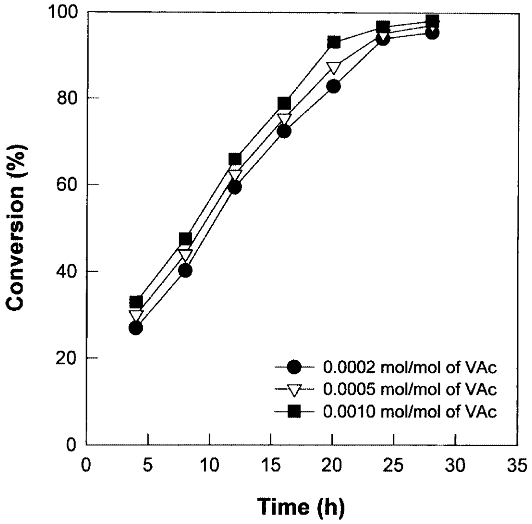

Fig. 1. Conversion of vinyl acetate (*VAc*) into poly(vinyl acetate) (*PVAc*) suspension polymerized at 50 °C using a suspending agent concentration of 0.5 g/dl in water, VAc/water of 0.5 l/l, and an agitation speed of 500 rpm with polymerization time

Results and discussion

The general PVA preparation process includes two steps using two different batches, but the continuous process involves saponification and polymerization in one batch. In this respect, the one-batch process is a very simple and effective method of preparation of PVA.

In this study we obtained PVAc with a high conversion of over 95% and the resultant HMW PVA using a one-batch continuous process. We obtained PVA beads with a spherical shape, but the particle size distribution of the PVA beads was somewhat irregular owing to preparation by the one-batch process using heterogeneous saponification.

The effect of the initiator concentration on the conversion of VAc into a PVAc suspension polymerized at 50 °C is shown in Fig. 1. The conversion rate increased as the ADMVN concentration increased, and a high conversion of over 95% was obtained at all ADMVN concentrations. This explains the fact that suspension process by ADMVN is a useful one for producing a high conversion of PVAc.

Plots of P_n of PVAc and PVA prepared by the one-batch process at three different polymerization temperatures are shown in Fig. 2a and b, respectively. The difference between the P_n of PVAc and PVA is mostly the result of branched structures, which may be broken down when saponified [2]. The P_n of PVA obtained using the continuous process with a high yield was over 5,000. The P_n of PVA increased as the polymerization temperature or the initiator concentration decreased. The P_n of PVA prepared by the two-batch process was 4,200–6,000. HMW PVA having P_n of 2,500–5,500 was prepared by the continuous process, and there was a little difference in the P_n of the PVA beads prepared by the two-batch process [17]. It should be noted that PVA with a P_n of up to 5,000 could be prepared by the one-batch process from PVAc polymerized at a conversion of 95% using an ADMVN concentration of 0.0002 mol/mol of VAc.

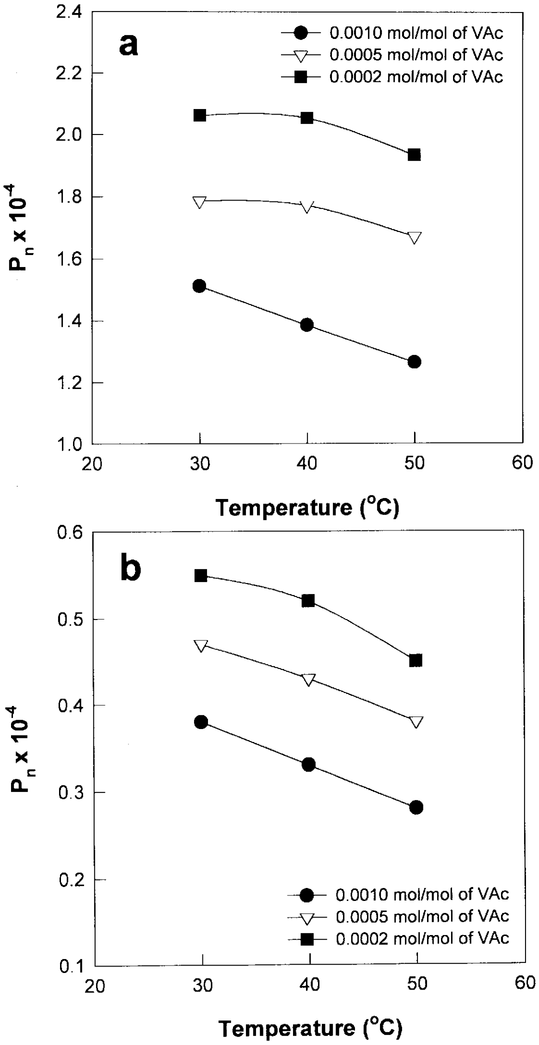

Fig. 2. P_n of **a** PVAc obtained by one-batch suspension polymerization at 50 °C using a suspending agent concentration of 0.5 g/dl in water, VAc/water of 0.5 l/l, and an agitation speed of 500 rpm and **b** PVA by saponification at 60 °C using alkali concentrations of 15/7.5/10 wt% ($NaOH/Na_2SO_4/CH_3OH$) in aqueous solution with polymerization temperature

In this study, the effects of the ADMVN concentration and the polymerization temperature on the DB of PVA were investigated. The variation of the DB for the acetyl group of PVAc polymerized at three different temperatures is shown in Fig. 3. All the specimens were obtained at similar conversions of about 90%. The DB increases as the ADMVN concentration and the poly-

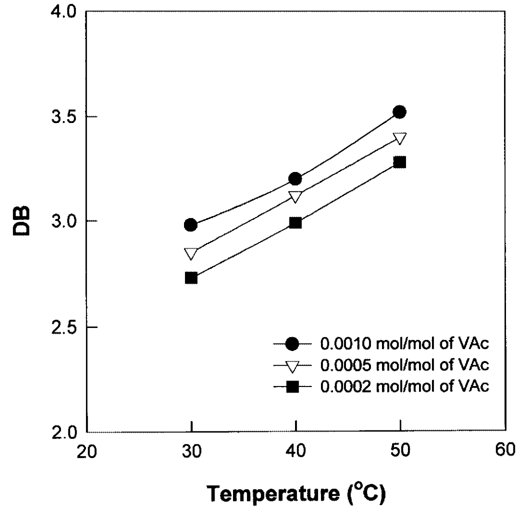

Fig. 3. DB for the acetyl group of PVAc obtained by suspension polymerization at three different polymerization temperatures using a suspending agent concentration of 0.5 g/dl of water, VAc/water of 0.5 l/l, and an agitation speed of 500 rpm

merization temperature increased. This may be ascribed to the fact that at higher polymerization temperatures, the accelerated polymerization reaction may bring about a chain-transfer (branching) reaction more easily [2]. In addition, it was supposed that the higher the initiator concentration, the more frequent the side reactions. Thus, the DB was increased. The DB of PVAc prepared in this study is 2.5–3.5.

The alkaline catalysts potassium hydroxide, gauanudine carbonate, sodium hydroxide and barum hydroxide are employed in the alcoholysis of PVAc [28, 29, 30]. Among them, sodium hydroxide is the most important catalysts for hydrolysis on an industrial scale. We used sodium hydroxide in one batch process. The dependence of the DS upon the saponification temperature at three different suspension polymerization temperatures is shown in Fig. 4a. The DS value was much higher at 60 °C than at 50 °C, which is because of the accelerated saponification reaction at higher temperature. The precursor preparation temperature had little effect on the DS of PVA. The DS of PVA prepared by the one-batch process was over 99% at a saponification temperature of 60 °C, and the PVA beads prepared were spherical. The dependence of the DS on the saponification time at two different saponification temperatures is shown in Fig. 4b. The DS increase as the saponification time increase. PVA saponified at 60 °C has a higher DS than that saponified at 50 °C. The maximum DS of PVA saponified at 50 °C was lower 95%, and was more influenced by the saponification temperature than the saponification time.

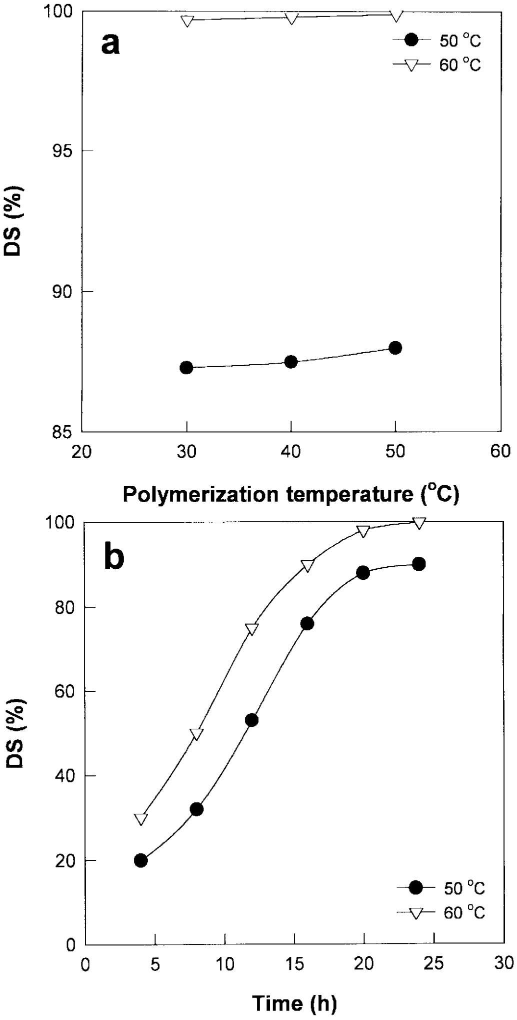

Fig. 4. **a** Degree of saponification (*DS*) of PVA with P_n of 5,000 prepared by one-batch polymerization and saponification at two different saponification temperatures using alkali concentrations of 15/7.5/10 wt% ($NaOH/Na_2SO_4/CH_3OH$,) in aqueous solution for a saponification time of 24 h with polymerization temperature and **b** DS of PVA with P_n of 5,000 prepared under the same conditions with saponification temperature

The dependence of the DS on the three different sodium hydroxide concentrations at saponification temperatures of 50 and 60 °C is shown in Fig. 5. The DS increase as the saponification temperature or the sodium hydroxide concentrations increased. The DS of PVA was over 99% at a saponification temperature of 60 °C for a sodium hydroxide concentration of 15 wt%. From this result, it was found that the effective concentration of sodium hydroxide for complete saponification at 60 °C is about 15 wt%.

The physical properties of PVA are influenced by the tacticity. The effects of the suspension polymerization temperature and the initiator concentrations on the s-diad content of PVA prepared by the one-batch and the general two-batch processes are shown in Table 1. In both processes, the s-diad content decreased as the polymerization temperature increased, but there was a little

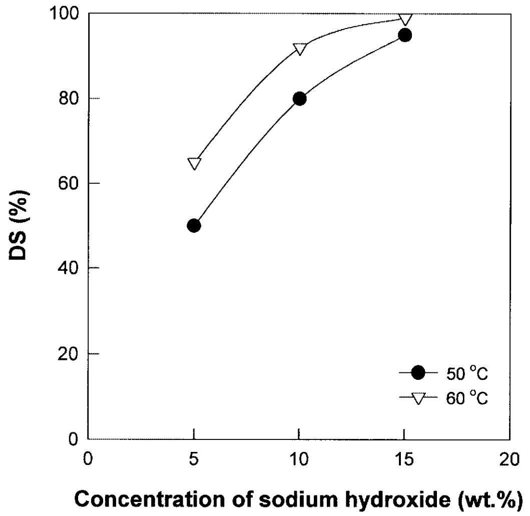

Fig. 5. DS of PVA with P_n of 5,000 prepared by one-batch polymerization and saponification at three different sodium hydroxide concentrations using a saponification time of 24 h

difference in the dependence of the s-diad contents on the polymerization temperature, arising from the atactic character of VAc polymerization. PVA with s-diad contents of 51–53% was obtained irrespective of the initiator concentration, and this was described as typically atactic PVA. The effects of the suspension polymerization temperature and the ADMVN concentrations on the T_m of PVA prepared by the one-batch and the general two-batch processes are also presented in Table 1. T_m increased as the polymerization temperature decreased, which agrees well with the tacticity data described previously. The negligible effect between the one-batch and the two-batch processes suggests that the shape and the size of the crystal are almost the same for the two PVA preparation processes.

Conclusions

As is well known, PVA cannot be obtained by direct polymerization owing to tauttomerism of vinyl alcohol monomer. We could prepare PVA by one-batch suspension polymerization and saponification. We adopted a suspension polymerization method, which is a powerful method for enhancing conversion. That is, we obtained spherical PVA beads using the continuous process. By using the one-batch process including suspension polymerization of VAc with ADMVN and continuous saponification, it is possible to produce HMW PVAc with a maximum conversion of VAc into PVAc of over 95% and HMW PVA with P_n of 2,500–5,500 and a DS of 85.0–99.9%. The P_n, DB, DS and s-diad content were not different from those of the general two-batch process. Conclusively, this one-batch suspension polymerization and saponification method is expected to be a simple and effective way of producing HMW PVA with high yield at low cost. Furthermore, the PVA microspheres in this study can be used as cancer cell-killing embolic materials. In the near future, we will report on the preparation of stereoregular PVA with high yield using one-batch suspension polymerization and saponification.

Acknowledgement This work was supported by a Korea Research Foundation grant (KRF-2000-041-E00417).

Table 1. Comparison of molecular parameters of poly(vinyl alcohol) prepared by one-batch and two-batch methods. T_{polym}, *m*, and *r* are the polymerization temperature, the isotactic diad content, and the syndiotactic diad content, respectively. *DS* is the degree of saponification

Method	2,2′-Azobis(2,4-dimethylvaleronitrile) concentration (mol/mol of vinyl acetate)	T_{polym} (°C)	P_n	DS (%)	*m* (%)	*r* (%)	T_m (°C)
One batch	0.0002	30	5,500	99.9	47.4	52.6	233.2
Two batch	0.0002	30	5,800	99.9	47.2	52.8	233.3
One batch	0.0010	30	4,500	99.9	47.4	52.6	232.9
Two batch	0.0010	30	4,600	99.9	47.3	52.7	233.2
One batch	0.0002	50	3,800	99.9	48.8	51.2	229.8
Two batch	0.0002	50	4,100	99.9	48.5	51.5	230.2
One batch	0.0010	50	2,800	99.9	48.7	51.3	229.9
Two batch	0.0010	50	3,100	99.9	48.2	51.8	230.3

References

1. Sakurada I (1985) In: Lewin M (ed) Polyvinyl alcohol fibers. Dekker, New York, pp 3–9, 361–36
2. Masuda M (1991) In: Finch CA (ed) Polyvinyl alcohol developments. Wiley, New York, pp 403–422, 711
3. Lyoo WS, Ha WS (1996) Polymer 37:3121
4. Lyoo WS, Blackwell J, Ghim HD (1998) Macromolecules 31:4253
5. Lyoo WS, Han SS, Choi JH, Cho YW, Ha WS (1995) J Korean Fiber Soc 32:1023
6. Lyoo WS, Ha WS (1999) Polymer 40:497
7. Lyoo WS, Chvalun SN, Ghim HD, Kim JP, Blackwell J (2001) Macromolecules 34:2615
8. Lyoo WS, Yeum JH, Ghim HD, Ji BC, Yoon WS, Kim JP (2000) J Korean Fiber Soc 37:487
9. Lyoo WS, Kim JH, Choi JH, Kim BC, Blackwell J (2001) Macromolecules 34:3982
10. Lyoo WS, Ha WS (1997) J Polym Sci Part A Polym Chem 35:55
11. Lyoo WS, Kim BJ, Ha WS (1996) J Korean Fiber Soc 33:231
12. Lyoo WS, Han SS, Choi JH, Ghim HD, Yoo SW, Lee J, Hong SI, Ha WS (2001) J Appl Polym Sci 80:1003
13. Lyoo WS, Ha WS (1996) J Korean Fiber Soc 33:156
14. Lyoo WS, Kim BC, Lee CJ, Ha WS (1997) Eur Polym J 33:785
15. Lyoo WS, Kwark YJ, Ha WS (1996) J Korean Fiber Soc 33:321
16. Kim SG, Lee WS, Jo SM, Kim BC, Lyoo WS, Han JR (1999) J Korean Fiber Soc 36:354
17. Lyoo WS, Lee SG, Kim JP, Han SS, Lee CJ (1998) Colloid Polym Sci 276:951
18. Sakurada I, Sakaguchi Y, Yamaguchi K (1963) Kobunshi Kagaku 20:491
19. Roberto O, Ernesto G, Bernardo G, Lorenzo S, Jesus A (1998) J Appl Polym Sci 67:71
20. Sandler SR, Karo W (1980) In: Blomqusit T, Wasserman H (eds) Polymer synthesis, vol 3. Academic, New York, pp 197–199, 211–217
21. Ma J, Chen L, He BJ (1996) J Appl Polym Sci 61:2029
22. Cherng-ju K, Ping IL (1992) J Appl Polym Sci 46:2147
23. Hayashi T, Hyon S, Cha W, Ikada Y (1993) Polym J 25:489
24. Varma S, Arvindakshan P, Bisarya S (1992) J Appl Polym Sci 46:02
25. Dionisoi JM, O'Driscoll KF (1980) J Polym Sci Part A Polym Chem 18:241–249
26. Yang C, Hamann H (1980) J Appl Polym Sci 25:2555
27. Murakami R, Hachisako H, Yamada K, Motozato Y (1992) Polym J 25:205
28. EI du Pont de Nemours and Co (1949) US Patent 2,464,290
29. EI du Pont de Nemours and Co (1949) US Patent 2,481,388
30. Firestone Tire and Rubber Co (1970) US Patent 3,494,908