

Synthesis and Characterization of Low Relative Molecular Weight *Trans*-1, 4-Poly(isoprene)

Huafeng Shao,¹ Baochen Huang,¹ Wei Yao,¹ Haixia Li²

¹Key Laboratory of Rubber-Plastic Ministry of Education, Qingdao University of Science and Technology, Qingdao 266042, China

²Qingdao double butterfly group Co. Ltd., Qingdao 266042, China

Received 18 June 2007; accepted 28 August 2007

DOI 10.1002/app.27355

Published online 6 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Low relative molecular weight *trans*-1,4-polyisoprene oligomers were synthesized successfully by bulk precipitation and solution polymerization with supported titanium catalyst using hydrogen as relative molecular weight modifier. The effects of polymerization conditions on intrinsic viscosity ($[\eta]$), catalyst efficiency (CE) and structure of polymer were studied. Increasing the hydrogen pressure resulted in the decrease of $[\eta]$ of the polymer. With the increasing of hydrogen pressure and reaction temperature, CE decreased but still maintained above 2500 g polymer/g Ti. The percentage composition of (*trans*-1, 4-unit) in the polymer was over 90% in all results. The crystallinity of

polymer was about 50–60% with T_m being about 60°C. The relative molecular weight distribution index (MWD) was quite difference according to the polymerization method. While number average molecular weight (M_n) exceeded 860, polymer turned from viscous materials to fragile wax materials, and then to toughness materials at 1800. Dynamic property testing showed that the additional of this oligomer could increase the wet-skid resistance of the rubber. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3734–3738, 2008

Key words: isoprene; supported titanium catalyst; coordination polymerization; hydrogen; oligomer

INTRODUCTION

With the development of fine chemistry, the application of low molecular weight polymer, also called oligomer, attracted more and more interests.^{1–3} Low relative molecular weight polyisoprene rubber was synthesized mostly by degradation of natural rubber and solid isoprene rubber or through free radical and anion polymerizations.^{4,5} All of these methods above could not control the molecular structure of products effectively, only obtained a miscellaneous structure of *cis*-1, 4-, *trans*-1, 4-, 3, 4-, and 1, 2-chain. The products usually were amorphous, liquid or viscous half-solid under room temperature, so called liquid rubber. Traditionally, the catalyst system of coordination polymerization could control the micro-structure effectively, but it is hard to control relative molecular weight. Shen and Tang and Yu^{6,7} synthesized isoprene trimer, which weight yield reached more than 81% by using complex titanium catalyst and the structure of these products was isoprene cyclic trimer. Huang et al. have synthesized high *trans*-1, 4- content of polyisoprene (TPI) using supported titanium catalyst $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(\text{i-Bu})_3$ through isoprene bulk precipitation polymerization.⁸

During the polymerization process, molecular weight of polymer decreased with the increasing of pressure of hydrogen.⁹ While the pressure of hydrogen increased up to a certain value, unsaturated wax which showed as crystalline solid under room temperature could obtain. The *trans*-1,4 content of the polymer reached more than 90%. Because of the micro-structure and physical property of the products, we called it low relative molecular weight *trans*-poly (isoprene) wax (LMTPIW) or oligomers. The as-synthesized oligomers have double bond which could vulcanize, and low melting point which made it an excellent mobility and operability. So it can be used as graining accessory ingredient during the rubber processing to avoid dust and pollution.

In this article, the effect of polymerization conditions on molecular weight, catalyst efficiency (CE), and structure of polymer was discussed. In bulk precipitation polymerization, MWD of polymer was wide because of the heterogeneous phase of the polymerization system. For the further study to reduce the MWD, we chose gasoline as solvent to realize solution polymerization.

EXPERIMENTAL

Materials

Commercially available isoprene (Ip, obtained from Shanghai Petro-Chemical, the purity was no less

Correspondence to: H. Shao (shaohf0826@msn.com).

than 99.5%) was dried by molecular sieves and purified by distillation to remove the inhibitor and water prior to polymerization. A supported Titanium catalyst ($\text{TiCl}_4/\text{MgCl}_2$) was prepared by our laboratory, the content of Ti is 1.8 wt %. Triisobutylaluminum (Al, polymerization grade) was diluted with gasoline to 2.148 mol L^{-1} . Pure hydrogen and antioxidant 2,6-bi-*tert*-butyl-4-methyl-phenol (BHT) were commercial products.

Polymerization

Bulk precipitation polymerization of Ip in the presence of the supported Ti catalysts was carried out in a sealed autoclave, filled with pure N_2 . A certain amount of Ip, Al, and Ti was added into the reactor in sequence. Hydrogen as chain transfer agent was kept at a given pressure during polymerization. The polymerization has two stages, the first stage was low-temperature prepolymerization for 1 h and then polymerized another 24 h with the desired temperature. The polymerization was terminated with quantitative alcohol, and antioxidant BHT was added in the reactor afterward at about 1 wt % of the product. After the unpolymerized monomer was removed, viscosity or wax polymer was obtained. The obtained polymer was weighed and calculated CE which used to express the activity of catalyst according to equation 1 below:

$$\text{CE} = \text{weight of obtained polymer (g)/catalyst (g)} \quad (1)$$

Solution polymerization of Ip was carried out as above except for the adding of gasoline as solvent. The concentration of Ip was about 50% (v : v).

Characterization

Gel content of the polymer was measured by gravimetry. The solid product ($\sim 0.1 \text{ g}$) was dissolved in an excess of toluene ($\sim 15 \text{ g}$) and stirred gently at 40°C for 30 h in darkness. The resulting solution was filtered using a $74 \mu\text{m}$ stainless steel filter. The unfiltered portion was weighed after drying in vacuum box.

T_m and crystallinity (X_c) were measured and recorded on a Shimadzu DSC-50 Differential Scanning Calorimeter with a heating rate at $10^\circ\text{C min}^{-1}$ (from 20 to 100°C). The calculation of X_c according to eq. (2):

$$X_o = (\Delta H/\Delta H^*) \times 100\% \quad (2)$$

where: ΔH , melting heat of as-obtained sample, J g^{-1} ; ΔH^* , melting heat of absolutely crystalline TPI which is 155.5 J g^{-1} .¹⁰

Microstructure analysis was examined using IR (Magna-IR Spectrometer, Nicolet) and $^{13}\text{C-NMR}$ (Mercury Plus 400 Nuclear Magnetic Resonance, Varian). Mole ratio of microstructure was calculated according to literature¹⁰ as follow:

$$C_{trans} = 23.1 \times D_{1152 \text{ cm}^{-1}} \quad (3)$$

$$C_{3,4} = 0.57 \times D_{890 \text{ cm}^{-1}} - 0.56 \times D_{1152 \text{ cm}^{-1}} \quad (4)$$

where: C_{trans} and $C_{3,4}$ represent the content of trans and 3,4-unit of TPI, and D represent the absorbance. 1152 cm^{-1} and 890 cm^{-2} in IR spectra represent the characterization peak of *trans* and 3,4-unit, respectively.

In $^{13}\text{C-NMR}$, Chemical shift of 23.6 ppm and 16.2 ppm represented the *cis*-1,4 and *trans*-1,4 unit characterization peaks respectively. The calculation of mole content used the characterization peaks area method.

M_n was determined by using QX-08 Vapor Pressure Osmometer at 50°C using bibenzoyl as standard sample.

Intrinsic viscosity $[\eta]$ was determined by Ubbelohde viscosimeter-one point method at a temperature of 30°C using toluene as solvent. $[\eta]$ and viscosity average molecular weight (M_η) were calculated as follow¹²:

$$[\eta] = 1.3714(\eta_{sp} - \ln\eta_r)^{0.5}/c(\text{dL g}^{-1}) \quad (5)$$

$$[\eta] = 7.35 \times 10^{-4} M_\eta^{0.697} \quad (6)$$

RESULTS AND DISCUSSION

Effects of polymerization conditions on $[\eta]$ and CE

In the experiment, Al/Ti and Ti/Ip mole ratio affect the $[\eta]$ slightly, so they are not the emphasis of our discussion. A common practice to reduce the average molecular weight is to introduce a chain-transfer agent. Hydrogen has been proved to be an effective agent.¹³ The experimental results show that hydrogen as a chain-transfer agent can adjust the molecular weight of TPI effectively. The effects of hydrogen pressure on $[\eta]$ of the oligomers are investigated, as shown in Figure 1.

It can be seen that $[\eta]$ of the oligomers obviously decrease with an increase in the H_2 pressure both solution and bulk precipitation polymerization. However, when hydrogen pressure increases to a critical value, $[\eta]$ of the oligomers decreases slightly with a further increase in the H_2 pressure. The appropriate H_2 pressure allows it to get oligomers with the desired molecular weight in the range of $[\eta]$ equal to 0.2–0.4 for solution polymerization and 0.2–0.6 dL g^{-1}

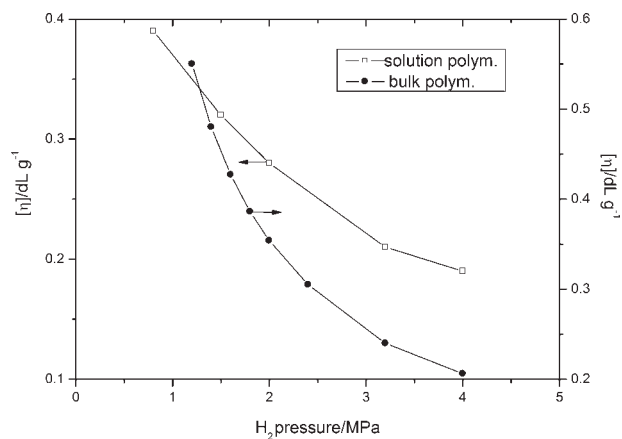


Figure 1 Effect of H₂ pressure on $[\eta]$ of the polymer obtained by solution and bulk precipitation polymerization ($n(\text{Ti})/n(\text{Ip}) = 8.10 \cdot 10^{-5}$, $n(\text{Al})/n(\text{Ti}) = 100$, $T = 20^\circ\text{C}$, $t = 24$ h).

for bulk precipitation polymerization, respectively. Compare with solution polymerization, with the increasing of H₂ pressure, the decrease of $[\eta]$ in bulk polymerization is intense. It also can be seen from Figure 1, at the same H₂ pressure, the $[\eta]$ of polymers by solution polymerization is lower than the one's by bulk polymerization. This may cause by the chain-transfer reaction to solvent during solution polymerization. This trend also occurs in the effect of temperature on the $[\eta]$ of oligomers, as shown in Figure 2. However, compare with H₂ pressure, the effect of temperature on $[\eta]$ is not obvious. With the increasing of temperature, the $[\eta]$ is increasing which differs from the general regulation of coordination polymerization due to the decreasing of the solubility of H₂ in the reaction system.

Although the increasing of H₂ pressure reduces the $[\eta]$ of the oligomers, it also lead to a reduction of CE, which shown in Figure 3. The effect of H₂ on

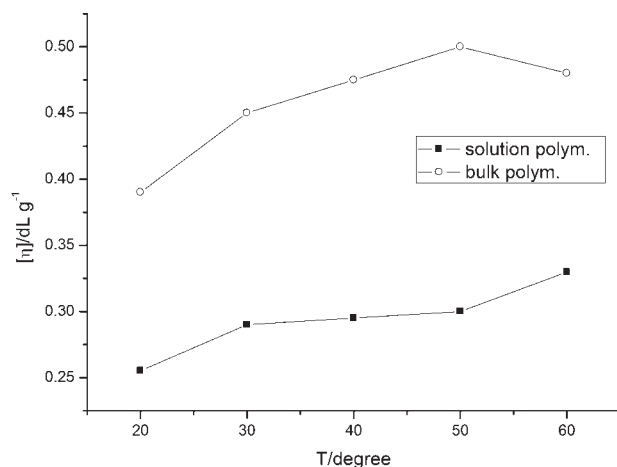


Figure 2 Effect of temperature on $[\eta]$ in solution and bulk precipitation polymerization ($n(\text{Ti})/n(\text{Ip}) = 5 \times 10^{-5}$, $n(\text{Al})/n(\text{Ti}) = 150$, $H_2 = 1.6$ MPa, $t = 24$ h).

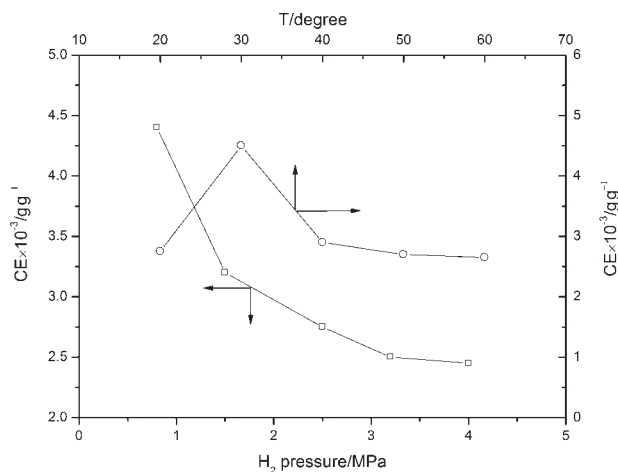
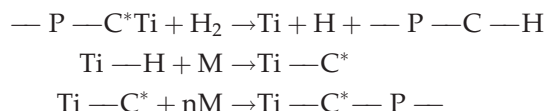


Figure 3 Effect of H₂ pressure and Temperature on CE in solution polymerization ($n(\text{Ti})/n(\text{Ip}) = 8 \times 10^{-5}$, $n(\text{Al})/n(\text{Ti}) = 100$, $t = 24$ h, $H_2 = 2.0$ MPa, $T = 20^\circ\text{C}$)

the $[\eta]$ of oligomers and CE could be explained by the following reaction mechanism¹⁴:



In this polymerization system, H₂ can transfer to Ti—C* active centers as a chain-transfer agent, and then Ti—H bonds and terminated polymer chains (—P—C—H) are formed. It is well known that, the Ti—H bonds are more stable than Ti—C* bonds, so more energy is needed for the Ti—H bonds to react with the monomer (M) to form the new Ti—C* bonds. Once the Ti—C* bonds are formed, they act as active centers and initiate monomers to propagate other polymer chains. Therefore, with the reduction of the $[\eta]$ of the oligomers, the whole polymerization rate is also reduced, that is to say, the CE is reduced but still above 2500 g polymer/g Ti while H₂ pressure is about 4 MPa. In bulk polymerization, reaction time prolong to 72 h, the CE can still maintain at 1.7×10^4 g polymer/g Ti while H₂ pressure is 1.6 MPa, and thus the $[\eta]$ is about 0.45 dL g⁻¹.

TABLE I
Mass Percent and M_n of Fraction

Fraction	Bulk polym		Solution polym	
	Mass percent, 100%	M_n	Mass percent, 100%	M_n
1	13.2	—	9.0	10,000
2	61.0	1809	9.5	2012
3	10.3	1436	17.0	782
4	8.3	1099	15.5	503
5	7.2	859	49.0	362

Polym. Condition: $n(\text{Ti})/n(\text{Ip}) = 8 \times 10^{-5}$, $n(\text{Al})/n(\text{Ti}) = 100$, $T = 20^\circ\text{C}$, $P_{H_2} = 4.0$ MPa, $t = 24$ h.

TABLE II
Melting Point and Crystallinity of Different Fractions of Bulk Polymerization by DSC

Fraction	Melting point (°C)	Crystallinity (%)
2	61.4	59.13
3	58.9	47.16
5	20.3	11.66

Molecular weight and MWD

Table I describes the mass percent and the corresponding number average molecular weight of solution and bulk polymerization respectively. The oligomers are classified by gasoline, toluene, and ethanol according to literature¹⁵ because of the different solubility of the different fractions of the oligomers in the three solvents and the solubility is determined by the relative molecular weight while the molecular structure is same.

From Table I, it can be seen that the mass percent of the fraction which M_n below 1000 is over 80% in solution polymerization and much more than the 7.2% in bulk polymerization. The value of M_n is determined by VPO method. After the data of both polymerizations were arranged and calculated according to literature,¹⁵ the obtained the MWD was 2.45 of solution polymerization and 1.1 of bulk polymerization. All analysis above demonstrates that solution polymerization could obtain oligomers with more less molecular weight and bigger MWD than by bulk polymerization under the same polymerization conditions.

Structure analysis

DSC

In Table II, the crystallinity of these fractions was calculated by peak area of the melting point. From Fig-

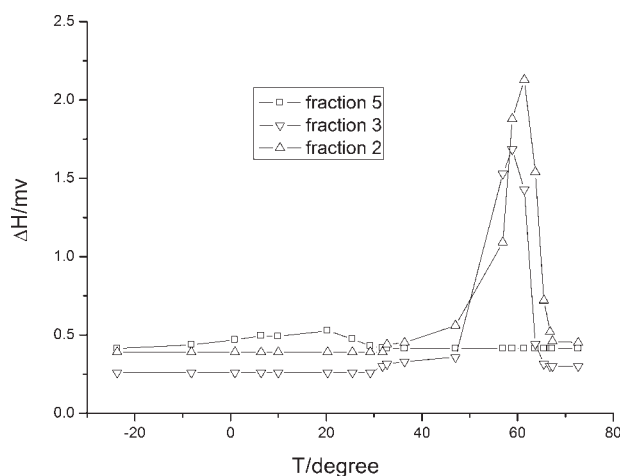


Figure 4 DSC curves of fraction 2, 3, 5 of bulk polymerization.

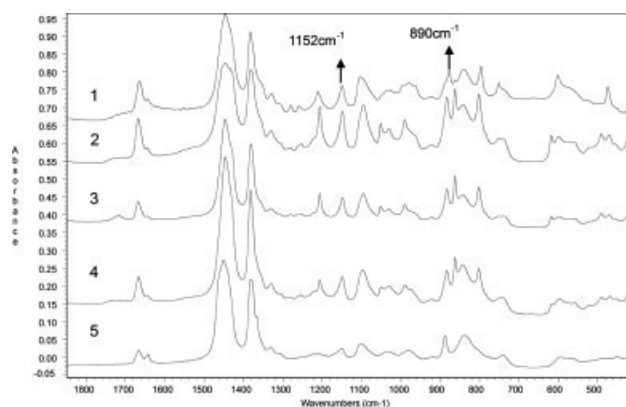


Figure 5 IR curves of different fractions of bulk polymerization.

ure 4 and Table 2, the crystallinity of fraction 2 and 3 is about 59 and 47% respectively and higher than the crystallinity of TPI.¹³ The high melting point and crystallinity of fraction 2 and 3 are due to the integrity of crystallization from diluted solution and the shorter segment which compared with TPI is easy to arrange and form a crystals. It also can be seen that the fraction 5 only has a crystallinity of about 12% with a melting point of about 20.3°C. Because the M_n of fraction 5 is only 860 which imply that fraction 5 has an average segment long of about 13, the crystallization of fraction 5 may be imperfect which bring it a low melting point. So, fraction 5 is a sticky fluid like aromatic oil in appearance. The appearance of fraction 2 and 3 is wax-like and higher molecular weight TPI is a kind of hard rubber.¹³ According to the relation of morphology and M_n above, it can be concluded that 860 and 1800 are the transition point of viscosity to brittleness and brittleness to toughness, respectively.

FTIR

IR spectra of fractions 1–5 are listed in Figure 5. In the region between 400 and 1600 cm^{-1} , a number of vibrations can be observed. The bands at 1152 and 890 cm^{-1} represent the trans 1,4-structure and 3,4-structure of Ip units, respectively.

TABLE III
Configuration Structure of Different Fractions of Bulk Polymerization

Fraction	Mole percent of 3,4-unit (by FTIR)	Mole percent of cis-1,4-unit (by ¹³ C-NMR)	Mole percent of trans-1,4-unit (by ¹³ C-NMR)
1	1.1	–	98.9
2	0.9	4.7	94.4
3	1.0	6.6	92.4
4	1.0	1.1	97.9
5	1.5	8.7	89.8

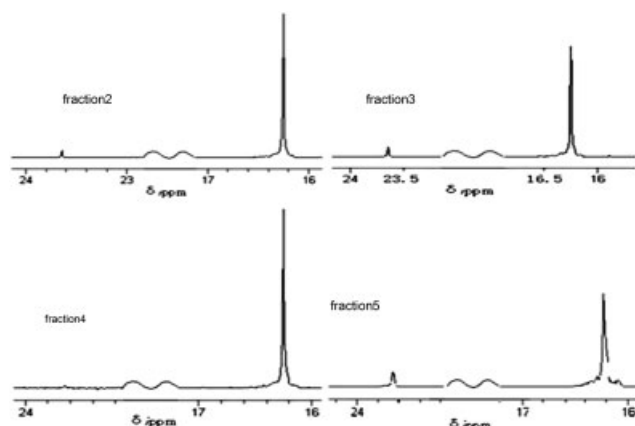


Figure 6 The ^{13}C -NMR spectra of different fractions of bulk polymerization.

The 3,4-structure of the oligomers are summarized in Table III according to the IR spectra. From Figure 5 and Table 3, it can be seen that only little content of 3,4-structure and without 1,2-structure. Because the characterization band of *trans*-1,4 and *cis*-1,4 is very close and hard to distinguish, ^{13}C -NMR is used to determine the content of the *cis*- and *trans*-configuration of the oligomers.

^{13}C -NMR

^{13}C -NMR spectra of the oligomers are shown in Figure 6. The content of the *cis*- and *trans*-structure obtained from ^{13}C -NMR spectra is shown in Table III. The content of *trans*-configuration is greater than 90% but lower than previous study¹³ may due to the direction ability of active center of this catalyst is decreasing under the high H_2 pressure.

Dynamic property

TPI oligomer can be used in tire formulation as a substitute for aromatic oil. Table IV lists the formulations. Figure 7 shows the $\tan \delta$ -temperature curves of different formulations. Generally, the $\tan \delta$ at 0°C can be used as an index to evaluate the wet-skid resistance of the tire. Rubber with higher $\tan \delta$ at 0°C has better wet-skid resistance. From Figure 7, $\tan \delta$ of formulation 1 is bigger than formulation 2 which indicate that its wet-skid resistance is better than formulation 2. So, TPI oligomers supplant the aromatic oil in the tire formulation can increase the wet-skid

TABLE IV

Formulation of the Dynamic Property Experiment (phr)

Formulation	1	2	3
SBR	100	100	80
TPI oligomer	20	0	20
TPI	0	0	20
Aromatic oil	0	20	0

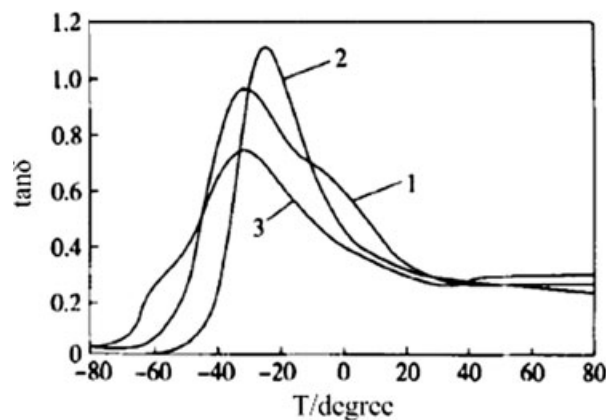


Figure 7 $\tan \delta$ -temperature curves of different formulation.

resistance obviously. We deduced the compatibility of TPI oligomers with SBR is better than aromatic oil because of similar of molecular main chain structure which bring it better wet-skid resistance.

CONCLUSIONS

In this article, low relative molecular weight high-*trans* 1,4-polyisoprene was synthesized with hydrogen as an effective molecular weight control agent in the presence of supported titanium catalysts. The relative molecular weight and CE were affected greatly by the polymerization such as H_2 pressure etc. M_n was decreased to about 860 while H_2 pressure was about 4.0 MPa. The percentage composition of (*trans*-1, 4-unit) in the polymer was over 90%. DSC showed the crystallinity of polymer was about 50–60% with T_m being about 60°C . The results of dynamic property showed that the additional of this oligomer could increase the wet-skid resistance of the rubber.

References

- Carpenter, J. F.; Roper, J. M. U.S. Pat. 5,207,940; 1993.
- Wu, M. M.; Chu, A. S. U.S. Pat. 5,276,227; 1994.
- Thomas, M. Adhes Age 1998, 41, 23.
- Zhang, Q. Y.; Han, X. Z.; Ji, K. J. Oligomer; Science Press: Beijing, 1994; p 75.
- Li, Z. F.; Wen, L. R.; Xu, C. M. Polym Mater Sci Eng 2003, 19, 126.
- Shen, G. L.; Tang, L. H. Speciality Petrochem 2004, 117, 1.
- Yu, S. J. Speciality Petrochem 2000, 3, 20.
- Huang, B. C.; He, J. D.; Song, J. S. ZL Pat. 95110352.0; 1995.
- Song, J. S.; Ma, Z. W.; Huang, B. C. China Syn Rubber Ind 2000, 25, 24.
- В.П.Привалко(Edr). Yan, J. B.; Zhang, Y. K. In (trans) Polymer Physical and Chemistry Handbook; China Petroleum Chemistry and Industry Press: Beijing, 1995; Vol. II, p 207.
- Cao, L. Y. Special Type Rubber Product 1987, 4, 20.
- Wu, Y. L.; Lu, Z. M. Chin Syn Rubber Ind 1989, 12, 185.
- Song, J. S.; Huang, B. C.; Yu, D. S. J Appl Polym Sci 2001, 82, 81.
- He, A. H.; Yao, W.; Huang, B. C.; Huang, Y. Q.; Jiao, S. K. J Appl Polym Sci 2004, 92, 2941.
- Zheng, C. R. Molecular Weight and Distribution of Polymer; Chemical Industry Publishing Company: Beijing, 1986; p 43.