

Studies on the Blends of Polycarbonate and Highly Branched Polystyrene

Ren Qiang, Li Aiyong, Jiang Bibiao, Zhang Dongliang, Chen Jianhai

Department of Material Science and Engineering, Jiangsu Polytechnic University Changzhou, People's Republic of China, 213016

Received 26 March 2004; accepted 12 July 2004

DOI 10.1002/app.21184

Published online 22 October 2004 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A highly branched polystyrene (HBPS) was synthesized via the copolymerization of 4-(chloromethyl)styrene with styrene using the self-condensing atom transfer radical polymerization method. The addition of this highly branched polystyrene as a melt modifier for polycarbonate (PC) was attempted. Indeed, the results show that the addition of highly branched polystyrene can decrease the melt viscosity of PC with little change in mechanical properties, although the blends do exhibit lower thermal stability com-

pared with pure PC. Extrapolation shows that all of the blends have an initial weight loss temperature above 450°C with a statistic heat-resistant index T_s above 225°C. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2425–2430, 2004

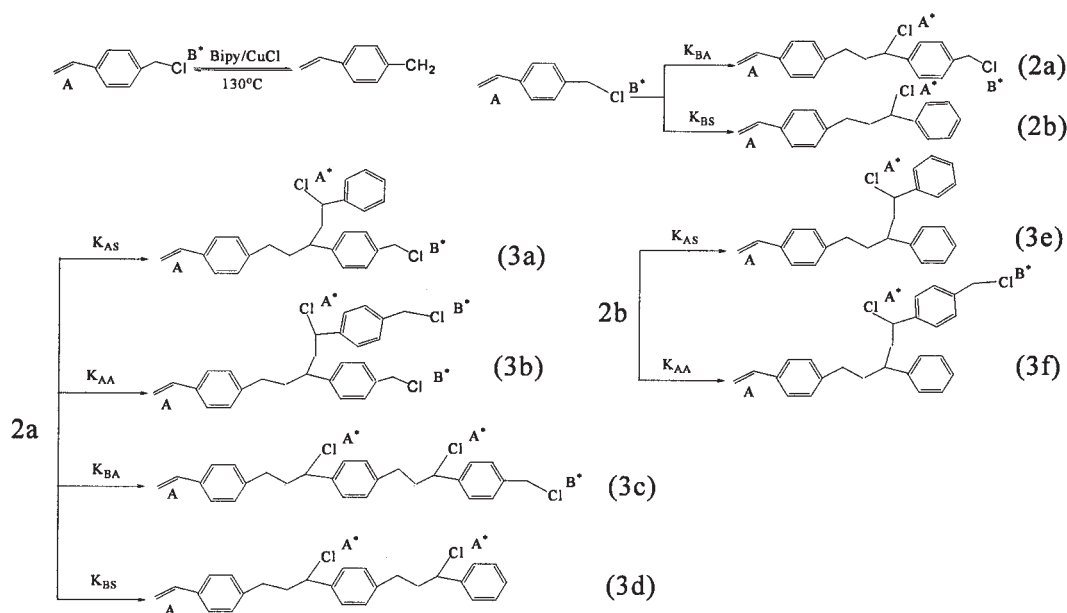
Key words: Atom transfer radical polymerization; highly branched polystyrene; polycarbonates; blending; melt modifier

INTRODUCTION

Dendrimers and hyperbranched polymers have received extraordinary scientific attention in recent years.^{1–16} Dendrimers are prepared in a multistep sequence with tedious isolation and purification procedures and accordingly have a precise molecular weight, topology, and surface reactivity, while hyperbranched polymers are prepared in a single step and have a less well-defined structure with polydisperse molecular weight, branching density, and number of end groups. Despite the differences between dendrimers and hyperbranched polymers, both have a highly branched “tree like” three-dimensional structure, which differentiates them from linear polymers. Accordingly, they do not have entangled chains, which results in a smaller hydrodynamic volume and lower melt viscosity than their linear analogues. Therefore, they can be expected to have value when employed as melt modifiers for plastics and coatings with high solids content. Furthermore, hyperbranched polymers have better industrial prospects than dendrimers because of their simple synthesis technique. In 1995, Kim and Webster¹⁷ first reported that the addition of a small amount of hyperbranched poly(phenylene) could decrease the melt viscosity of polystyrene, obviously with a concomitant sacrifice in the maximum tensile strength. Schmaljohann et al.¹⁸ studied the

blends of hyperbranched polyesters modified with dodecanoyl chloride and different polyolefins and found that the complex melt viscosity of the blends was lower than that predicted by the additive effect of the linear mixing rule with little change in the dynamic mechanical behavior. Massa et al.¹⁹ studied the phase behavior and mechanical properties of blends of both hydroxy-terminated and acetate-terminated all-aromatic hyperbranched polyesters with a variety of linear polymers. They found that the blends showed increased tensile and compressive moduli but decreased strain-to-break and toughness compared to unmodified PC. Hong et al.²⁰ investigated the use of a dendritic additive from Sweden Perstorp Specialty Chemicals as a processing aid for linear low-density polyethylene in a tubular film blowing process. Through the addition of one dendritic additive, “sharkskin” was successfully eliminated and the processing rate was enhanced. Mulkem and Tan²¹ studied a series of blends of hyperbranched polyesters terminated by hydroxyl group with high molecular weight polystyrenes and found that a significant drop in the blends viscosity occurs immediately upon addition of hyperbranched polyesters. It can be noted that all the aforementioned reports employed hyperbranched polymers prepared by a polycondensation method proposed by Flory²² in 1952 and most of them are hyperbranched polyesters. Since Fréchet and coworkers¹ first reported the synthesis of hyperbranched polymers by self-condensing vinyl polymerization in 1995, the species of hyperbranched polymers have been extended greatly and hyperbranched polymers

Correspondence to: J. Bibiao (jbb123@public.cz.js.cn).



Scheme 1 Schematic representation of the self-condensing vinyl copolymerization of CMS and styrene catalyzed by CuCl and Bipy. The chlorine atom can transfer with CuCl and Bipy catalysis, forming a radical. k_{AS} , k_{AA} , k_{BA} , and k_{BS} represent the reaction rate constant of A^* to St, A^* to CMS, B^* to CMS and B^* to St, respectively.

based on styrene, styrene derivatives,^{1,3,23} and acrylates^{4,5} all have been prepared.

Unfortunately, crosslinking is difficult to prevent in self-condensing atom transfer radical polymerization to synthesize hyperbranched polymers with high molecular weight from inimer (self-initiating monomer) of AB^* structure, in which A represents a double bond and B^* represents an alkyl halide functional group such as 4-(chloromethyl) styrene (CMS).²³ The crosslinking tendency is derived from radical–radical coupling reaction. Since the number of carbon–halogen bonds is equal to X_n in the product prepared by the SCVP of inimer of AB^* structure,⁵ the macromolecules with higher X_n would undergo the crosslinking reaction easily because of having more radicals in the molecules. In our study, styrene was employed to copolymerize with 4-(chloromethyl) styrene. It is expected that the crosslinking reaction can be avoided and highly branched polystyrene with high molecular weight will be prepared because of fewer radicals in the resulting macromolecules. The product undoubtedly has a lower degree of branching compared with

the polymer prepared by the homopolymerization of CMS and is hence called “highly branched” rather than “hyperbranched” polystyrene. A small amount of the resulting highly branched polystyrene was added to PC and the effects on melt viscosity, mechanical properties, and thermal stabilities of the blends were investigated.

EXPERIMENTAL

Reagents

4-(Chloromethyl) styrene from Aldrich Chemical was washed with a 5% NaOH solution followed by distilled water three times and then dried using anhydrous Na_2SO_4 prior to use. Styrene, an analytical reagent from Shanghai No. 1 chemical reagent factory, was distilled under reduced pressure. 2,2'-Bipyridyl (Bipy), an analytical reagent, was used as received from Shanghai No.1 chemical reagent factory. Copper(I) chloride (CuCl , AR grade) was purified by stirring in acetic acid, washing with methanol, and then

TABLE I
Molecular Weights of HBPS Determined by GPC and MALLS

HBPS	Mole ratio of CMS to St	Yield (%)	$M_{n,GPC}$	$M_{w,GPC}$	$\frac{M_{w,GPC}}{M_{n,GPC}}$	$M_{w,MALLS}$
HBPS-1	1:20	75	30,129	78,084	2.59	138,400
HBPS-2	1:15	81	16,552	58,003	3.50	127,100
HBPS-3	1:10	85	19,368	81,129	4.19	181,800

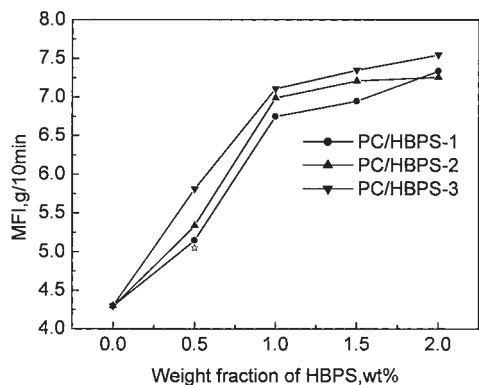


Figure 1 MFI of PC and blends of HBPS and PC. ☆, The replicate data of PC/HBPS-1 with 0.5% HBPS to assess the reproducibility of the data.

drying under reduced pressure. Polycarbonate, Bayer 310-7, was dried under reduced pressure before use.

Synthesis of highly branched polystyrene

In a typical polymerization, CMS (1.22 g, 8 mmol), styrene (8.32 g, 80 mmol), Bipy (0.374 g, 2.4 mmol), and CuCl (0.118 g, 1.2 mmol) were added into a dry 100-mL round-bottom flask equipped with a PTFE stirring bar. The flask was cycled between vacuum and nitrogen > 10 times to remove the oxygen. The flask was then sealed and placed in a preheated, thermally regulated oil bath at $130 \pm 1^\circ\text{C}$. After 24 h polymerization under stirring, the flask was removed from the oil bath and allowed to cool for a few minutes. Butanone (50 mL) was added into the flask to dissolve the product: all of the product can be dis-

solved without any gel. The solution was then filtered to separate the salt from the catalyst. Ethanol (5 times the butanone volume) was added to the filtrate to precipitate the polymer. After repeating the dissolution and precipitation processes a second time, the polymer was dried at 40°C under reduced pressure to yield the highly branched polystyrene (yield: 85%).

Blending with PC

Typically, 2 g of powder of highly branched polystyrene was added to 100 g of molten PC at 250°C in a Banbury mixer and mixed for 5 min. For comparison, pure PC was treated in the same way as the blends.

Characterization methods

Gel permeation chromatography (GPC) was performed on a GPC line consisting of a Waters 1515 Isocratic HPLC Pump, Waters styragel HR 4e, HR 1 and HR 0.5 column, and a Waters 2414 Refractive Index Detector at room temperature. The eluent was tetrahydrofuran with a flow rate of 1 mL/min and the data were obtained with linear polystyrene standards. Multiangle laser light scattering (MALLS) was conducted on 703-T mini DAWN Tristar Light Scattering Photometer. Differential scanning calorimetry (DSC) was performed on a PE-7 thermal analysis system under N_2 atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. The sample and reference pan had the same mass within $\pm 0.5\text{mg}$ of each other. Thermal gravimetry analysis (TG) and derivative thermal gravimetry (DTG) were carried out on a SDTQ-600 thermalgravimetric analyzer under N_2 atmosphere in the temper-

TABLE II
Mechanical Properties of the Blends and Pure PC

Sample	HBPS	HBPS/PC (wt %)	A Tensile strength ^a		B Elastic modulus ^a		C Izod impact ^a	
			(MPa)	S^b (A)	(MPa)	S^b (B)	strength (J/m)	S^b (C)
PC		0	66.2	0.23	2,040	0.019	54.8	0.24
1	HBPS-1	0.5	66.8	0.28	2,110	0.024	57.1	0.22
2 ^c	HBPS-1	0.5	66.4	0.25	2,090	0.028	62.2	0.24
3	HBPS-1	1.0	66.2	0.24	2,060	0.042	98.4	0.40
4	HBPS-1	1.5	67.1	0.35	2,060	0.036	52.8	0.26
5	HBPS-1	2.0	69.7	0.21	2,070	0.029	48.0	0.30
6	HBPS-2	0.5	67.8	0.38	2,070	0.027	58.4	0.28
7	HBPS-2	1.0	68.4	0.42	2,060	0.034	64.8	0.23
8	HBPS-2	1.5	66.7	0.24	2,100	0.028	49.1	0.25
9	HBPS-2	2.0	67.3	0.31	2,060	0.031	46.3	0.28
10	HBPS-3	0.5	66.2	0.25	2,070	0.030	87.2	0.35
11	HBPS-3	1.0	66.2	0.26	2,060	0.035	55.7	0.31
12	HBPS-3	1.5	67.3	0.32	2,070	0.027	47.4	0.28
13	HBPS-3	2.0	66.8	0.30	2,060	0.025	44.8	0.25

^a The arithmetic mean of five specimens, \bar{X} ,

^b $S = (\sum X^2 - n\bar{X}^2)/(n - 1)$ where S = estimated standard deviation, X = value of single observation, n = number of observation and is 5 here, \bar{X} = arithmetic mean of the set of observation.

^c Replicate data of sample 1 to assess the reproducibility of the data.

TABLE III
Measured T_g of HBPS and Pure PC

Sample	Mass of the sample (mg)	ΔC_p (J/g · °C)	T_g (°C)
PC	7.856	0.310	149
HBPS-1	8.578	0.573	90
HBPS-2	7.230	0.550	89
HBPS-3	9.640	0.649	92

ature range of 100–700°C, at a heating rate of 10°C/min. The melt flow index (MFI) of blends was determined on a XLR400 MFI instrument from the Chemical Instrument Factory of Jilin University at 275°C with a load of 1.05 kg. Tensile properties measurement was performed according to ASTM D 638–90. Impact resistance properties measurement was performed according to ASTM D 256–90b. Five specimens were tested for each sample.

RESULTS AND DISCUSSION

Self-condensing copolymerization of CMS and styrene

All of the monomers used in the self-condensing vinyl radical polymerization have an AB^* structure, in which A represents a double bond and B^* represents an alkyl halide functional group. B^* is chloromethylbenzene in CMS. Scheme 1 shows the reaction sequence for the self-condensing vinyl copolymerization of CMS with styrene when catalyzed by CuCl and Bipy. The methylstyrene radical resulting from the transfer of chlorine atom can initiate the double bond of the CMS to form dimer 2a, which has two initiating centers, A^* and B^* . The chain propagation occurring at A^* will result in the formation of a trimer having a

branched structure, such as 3a and 3b. However, the methylstyrene radical can also initiate the double bonds of styrene to form dimer 2b, which has only one initiating center, A^* . Chain propagation of species 2b can only occur at this center to produce a linear structure. Thus, if a single molecule of CMS is involved in the propagation, an initiating center is added to the chain and a branch point can be expected. It is obvious that the degree of branching will be directly related to the rate constants k_{AS} , k_{AA} , k_{BA} , and k_{BS} . That is to say, if more CMS is employed in the polymerization, the resulting hyperbranched polymer will have a higher degree of branching than if less CMS is used.

The molecular weights of the resulting highly branched polystyrene, determined by GPC and MALLS, are shown in Table I. It can be seen that the molecular weight determined by MALLS is much larger than that determined by GPC. Branched polymers have smaller hydrodynamic volumes than their linear analogues,²⁴ which leads to longer retention times in the GPC and, consequently, apparently show lower molecular weight values than their actual values obtained from other methods, such as ¹H-NMR and MALLS. The differences in molecular weight shown in Table I show that these polymers have branched structures as expected. Furthermore, all of the products have a yield above 75% and no crosslinking reaction was observed in the polymerization process.

MFI of blends

The MFI of all the blends was measured to study the effect of the addition of highly branched polystyrene on the properties of PC. As shown in Figure 1, the MFI increases with the weight fraction of highly branched polystyrene. At a given weight fraction of highly

TABLE IV
Measured T_g versus Calculated T_g Using the Fox Equation for Blends

Sample	HBPS	Weight fraction of HBPS in blends (wt %)	Mass of the sample (mg)	ΔC_p (J/g · °C)	Measured T_g (°C)	Fox T_g (°C)
1	HBPS-1	0.5	9.524	0.796	150	149
2 ^a	HBPS-1	0.5	8.150	0.531	150	149
3	HBPS-1	1.0	7.138	0.484	149	148
4	HBPS-1	1.5	8.756	0.290	147	148
5	HBPS-1	2.0	6.540	0.475	148	147
6	HBPS-2	0.5	7.857	0.367	150	149
7	HBPS-2	1.0	9.160	0.319	149	148
8	HBPS-2	1.5	6.458	0.494	149	147
9	HBPS-2	2.0	6.690	0.281	148	147
10	HBPS-3	0.5	7.325	0.421	149	149
11	HBPS-3	1.0	8.780	0.311	150	148
12	HBPS-3	1.5	9.850	0.359	149	148
13	HBPS-3	2.0	8.230	0.306	148	147

^a Replicate data of sample 1 to assess the reproducibility of the data.

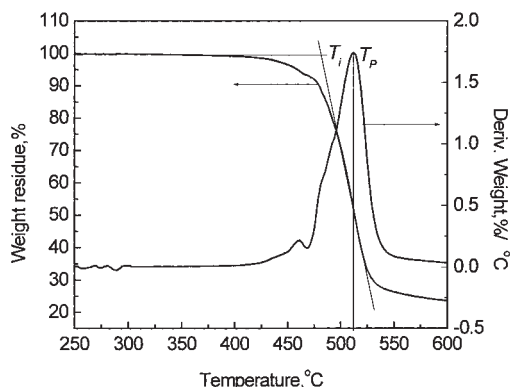


Figure 2 TG and DTG thermograms of sample 4 as a representative of the blends of HBPS and PC. Initial weight loss temperature T_i is the temperature corresponding to the point of intersection of the baseline and the tangent line at T_p . T_p is the temperature with the fastest weight-losing rate determined by DTG.

branched polystyrene as concerned, the MFI increased as the degree of branching of the highly branched polystyrene increases. It can be concluded that the addition of highly branched polystyrene can decrease the melt viscosity of PC and that a highly branched polystyrene having a higher degree of branching shows somewhat higher modification efficiency. The lower viscosity resulted from the lubricating ability of HBPS, which has a highly branched, three-dimensional structure without entangled chains.

Mechanical properties of blends

In addition to their ability to function as a melt modifier, the influence on the mechanical properties of the

PC blends is also important, as shown in Table II. It can be seen that all of the blends showed no apparent difference in tensile strength and izod impact strength compared with pure PC, but a small increase in the elastic modulus was observed. The higher elastic modulus compared with pure PC is consistent with the aromatic character of polystyrene added in the blend, which is similar to the result reported by Massa et al.¹⁹ All of the standard deviations in Table II vary within an acceptable range, which verifies the statistical significance of the data.

Differential scanning calorimetry analysis

The T_g s of the highly branched polystyrene, the PC, and their blends are shown in Table III and IV. The Flory–Fox equation is widely used to predict the T_g of blends. The calculated T_g s of the blends, obtained from this equation, are also given in Table IV. It can be seen that the measured values are in agreement with the calculated values. The T_g s of the blends are not significantly different from that of pure PC because of the low weight fraction of highly branched polystyrene in the blends.

The Flory–Fox equation is as follows:

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \quad (1)$$

where ω_i is the weight fraction of the component i .

Thermal gravimetry analysis

As shown in Figure 2 and Table V, most of the blends show an extrapolated onset of weight loss at a lower

TABLE V
TG Results of Pure PC and Blends of HBPS and PC

Sample	HBPS	HBPS/PC (wt %)	T_i^a (°C)	T_5^b (°C)	T_{30}^b (°C)	T_5^b (°C)
PC		0	478	463	496	237
1	HBPS-1	0.5	466	459	487	233
2 ^c	HBPS-1	0.5	470	455	506	238
3	HBPS-1	1.0	464	460	487	232
4	HBPS-1	1.5	484	461	501	238
5	HBPS-1	2.0	462	444	482	229
6	HBPS-2	0.5	476	459	499	235
7	HBPS-2	1.0	473	454	493	234
8	HBPS-2	1.5	466	446	487	230
9	HBPS-2	2.0	472	446	489	231
10	HBPS-3	0.5	486	470	501	240
11	HBPS-3	1.0	501	482	513	245
12	HBPS-3	1.5	453	441	472	225
13	HBPS-3	2.0	454	444	475	227

^a Initial weight loss temperature from extrapolation methods as shown in Figure 2.

^b T_5 , T_{30} : temperature of 5% and 30% weight loss; $T_5 = 0.49[T_5 + 0.6(T_{30} - T_5)]$.

^c Replicate data of sample 1 to assess the reproducibility of the data.

temperature than pure PC. The decrease in thermal stability is probably due to the labile carbon–chlorine bonds of the highly branched polystyrene. The highly branched polymers with numerous carbon–halogen end groups have a lower initial weight loss temperature than their linear analogues.^{11,23} But the decrease in thermal stability of the blends is trifling and all the blends still have extrapolated initial weight loss temperatures above 450°C and a statistic heat-resistant index T_s above 225°C, which do not affect the temperature-resistant property of PC substantially.

CONCLUSION

We have synthesized a highly branched polystyrene from the copolymerization of CMS with styrene using the self-condensing atom transfer radical polymerization method. No crosslinking reaction occurred in the polymerization process. We have shown that the addition of a small amount of this highly branched polystyrene can decrease the melt viscosity of the blend. When the more highly branched polystyrene is employed, there is a greater increase in the MFI of the blend. The addition of highly branched polystyrene has little effect on the mechanical properties, although the blends have a lower thermal stability than pure PC. These blends can be processed with a lesser energy input than pure PC due to the decreased viscosity.

This work was supported by the National Science Foundation of China and the Youth Foundation of Jiangsu Province.

References

- Fréchet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* 1995, 269, 1080.
- Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J Am Chem Soc* 1995, 117, 10763.
- Scott, G. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* 1996, 29, 1079.
- Matyjaszewski, K.; Kulfan, A.; Podwika, M. *Macromolecules* 1997, 30, 5192.
- Matyjaszewski, K.; Scott G. G.; Müller, A. H. E. *Macromolecules* 1997, 30, 7034.
- Matyjaszewski, K.; Scott G. G. *Macromolecules* 1997, 30, 7042.
- Matyjaszewski, K.; Wang, J. L.; Grimaud, T.; Shipp, D. A. *Macromolecules* 1998, 31, 1527.
- Wang, J. L.; Grimaud, T.; Matyjaszewski, K. *Macromolecules* 1997, 30, 6507.
- Ambade, A. V.; Kumar, A. *Prog Polym Sci* 2000, 25, 1141.
- Jikei, M.; Kakimoto, M. A. *Prog Polym Sci* 2001, 26, 1233.
- Jiang, B. B.; Yang, Y.; Deng, J.; Fu, S. Y.; Zhu, R. Q.; Hao, J. J.; Wang, W. Y. *J Appl Polym Sci* 2002, 83, 2114.
- Müller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* 1997, 30, 7015.
- Yan, D.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7024.
- Yan, D.; Zhou, Z.; Müller, A. H. E. *Macromolecules* 1999, 32, 245.
- Mori, H.; Böker, A.; Krausch, G.; Müller, A. H. E. *Macromolecules* 2001, 20, 6871.
- Khan, M.; Huck, W. T. S. *Macromolecules* 2003, 36, 5088.
- Kim, Y. H.; Webster, O. W. *Macromolecules* 1992, 25, 5561.
- Schmaljohann, D.; Pötschke P.; Hässler, R.; Voit, B. I.; Froehling, P. E.; Mostert, B.; Loontjens, J. A. *Macromolecules* 1999, 32, 6333.
- Massa, D. J.; Shriner, K. A.; Turner, S. R.; Voit, B. I. *Macromolecules* 1995, 28, 3214.
- Hong, Y.; Coombs, S. J.; Cooper-White, J. J.; Mackay, M. E.; Hawker, C. J.; Malmström, E.; Rehnberg, N. *Polymer* 2000, 41, 7705.
- Mulkern, T. J.; Tan, N. C. B. *Polymer* 2000, 41, 3193.
- Flory, P. J. *J Am Chem Soc* 1952, 74, 2718.
- Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J Polym Sci Polym Chem* 1998, 36, 955.
- Grubisic, Z.; Rempp, P.; Benoit, H. *J Polym Sci Polym Lett* 1967, 5, 753.