Archive of SID

Polystyrene Star-shaped Polymers Made by the New "In-In" Method

Naghmeh Fazeli and Faramarz Afshar Taromi *

Department of Polymer Engineering, Amir Kabir University of Technology, Tehran, I.R. Iran

ABSTRACT

Three main methods are usually used for the synthesis of star-shaped polymers, where each one has its own advantages and disadvantages. Among these techniques, "in-out" method is the best one to produce hetero-arm star polymers with narrow molecular weight distribution and long arms with active sites at the end of the second-generation arms. This method, however, has some difficulties during the synthesis of hetero-arm star polymers with styrene or dienes as the second monomers. The reason is that in the "out" step, the carbanions of the growing chains attack the existing double bonds of the other cores and produce an irreversible gel. The new "in-in" method mentioned in this paper, is used to synthesize double-star polystyrene polymers with relatively narrow molecular weight distribution and without occurrence of any gelation during the process. With the monomers, which are able to attack the existing double bonds of the cores of the star polymers, it is also possible to produce hetero-arm star polymers using this new method.

Key Words: double-star polymer, hetero-arm star polymer, living chain, carbanion, gelation

INTRODUCTION

Until recently, there have been three main methods for the synthesis of star-shaped polymers via anionic polymerization. Deactivation method, which is reported by Morton et al. in 1962 [1], involves the reaction of living polymeric monoanions with the exact or slightly less stoichiometric proportions of a multi-functional linking agent with antagonist functions (deactivator) to form star branched polymers. This

method, which is considered as a type of arm-first method, has been applied in the synthesis of homostar [1,2] and hetero-arm [3,4] star polymers.

Arm-first method involves reaction of mono-carbanionic precursor chains as the initiator for the polymerization of a small amount of a bis-unsaturated monomer such as divinylbenzene (DVB). This procedure was mentioned first by Milkovich in 1965, and later it developed extensively by others [6,7]. In this method, upon a three-step mechanism [8,9], small,

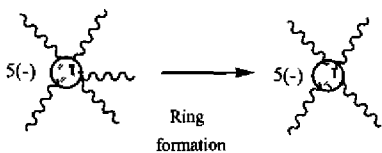(*) To whom correspondence should be addressed. Email: f7332958@cic.aku.ac.ir

www.SID.ir

tightly cross-linked nodules of poly (DVB) are formed where each one is connected to the well–characterized precursor chains that have initiated the DVB polymerization (Scheme I).
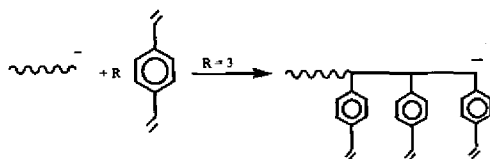
Formation of linear block copolymers

Cross-linking

Ring formation
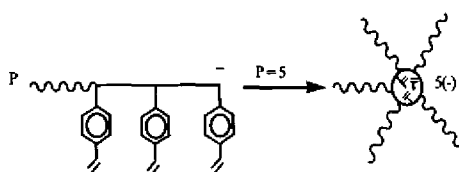
Scheme I

The branches protect the cores to prevent cross-linking between individual star molecules, unless the cores constitute more than 40 wt % of the star molecule [10]. This method was used successfully for the preparation of star polymers exhibiting elastomeric branches (polybutadiene and polyisoprene) and also star block-copolymers of polystyrene-polydiene [11,12].Core-first method, which has been described by Eschway and Burchard in 1975 [8], and later by Lutz and Rempp [13], involves the in situ formation of a multifunctional anionic initiator by the reaction of a divinyl compound such as divinylbenzene (DVB) with an anionic initiator in dilute solution. This method has been used for synthesizing homostar polymers of poly (ethylene oxide) [14,15], polystyrene [13] and star block copolymers of polystyrene-poly-butyl methacrylate [16].

In-out method, which has been mentioned by Afshar Taromi and Rempp in 1989 [10], and then extensively developed by others [17-19], is a combination of the last two mentioned methods. In other words, first a living precursor (such as poly-styrene) initiates the polymerization of a small amount of DVB, where the cores are formed as in an "arm-first" process. Subsequently the active sites located in the cores are used to initiate the polymerization of another suitable monomer such as ethylene oxide [15,20], alkyl methacrylate [21], *t*-butyl acrylate [18], 2-vinyl pyridine [22] and etc., whereupon a new set of branches, with active sites at their end, is generated from the cores. It should be noted that if the active sites of the second-generation branches can attack the unreacted existing double bonds of the core of the star molecules (such as in styrene or dienes), an irreversible gelation occurs [10]. Rein et. al. [19] have tried to overcome this problem by adding *sec*-BuLi to polystyrene star-shaped polymers, synthesized with arm-first method. In this way, the number of the residual double bonds of the cores is efficiently reduced through the reaction with BuLi. However, as mentioned by the researchers, the unreacted BuLi produces free active sites outside of the cores, which is a drawback for the synthesis of double-star polymers.

The objective of this work is to synthesize polystyrene double-star polymers, without any gelation during the production. For this purpose a two-step method named "in-in" method is adopted. In the first step a polystyrene star polymer with poly (DVB) core is synthesized by arm-first method. In the second step after producing the living polystyrene chains, a known amount of the star polymer synthesized and characterized in the first step is dissolved in THF and added to the system. Thus a double-star polymer is synthesized and later it is characterized.

EXPERIMENTAL

Solvents and Reagents

Tetrahydrofuran (Merck, molecular weight 72.11, 99 % pure) was distilled over sodium wire. The blue colour of THF included sodium wire and a small

amount of benzophenone was an indicator for the lack of the protonic impurities. Divinylbenzene (once) and styrene (twice) were distilled under vacuum, over sodium wire. Divinylbenzene used (Merck, molecular weight 130.1) contained roughly 65 % of DVB and 33 % ethylvinylbenzene. n-Butyl lithium (Merck, molecular weight 64.06, solution 15 % in n-hexane) was used as initiator in the experiments and its molarity was determined by titration with acetanilide (Merck, molecular weight 135.17, 99 % pure).

Apparatus

The reaction was carried out in a 1 L reactor, fitted with magnetic stirrer, pure argon inlet, temperature control, burettes containing the solvent and monomers to be added, and a sampling device. The apparatus was designed to operate under a slight argon over-pressure, allowing all the reaction steps to be carried out under exclusion of air and moisture.

Synthesis

The experiments were performed in two steps.

Synthesis of Star Polymer as an Arm-first Method

The experiments were run in tetrahydrofuran (THF) solution at -30 °C. n-Butyl lithium (BuLi) was the initiator for synthesis of living polystyrene chains. The mole ratio of styrene monomer to the initiator was chosen to produce polystyrene chains with molecular weight of 4000-8000. A fraction of living polystyrene solution was sampled out for purpose of characterization. Then a known amount of divinyl-benzene (DVB), three times diluted in distilled THF, was added at once to the system with efficient stirring. The mole ratio of DVB to BuLi was about 10. The polymerization of DVB was conducted under the same conditions as that of styrene. The active sites of the star polymer formed were deactivated with methanol. Then the solution was precipitated and dried to form a fine white powder.

Synthesis of Double-star Polymer

First the precursor living polystyrene chains were synthesized with anionic polymerization. A fraction of solution was then sampled out for characterization.

Then 2 g of star polymer, synthesized and character-ized in previous step was dissolved in THF and added to the system. The system was stirred for a while and later the active sites were killed with methanol and the solution was precipitated in methanol and dried.

The samples were characterized by light scatt-ering (LS), size exclusion chromatography (SEC), viscometry and UV spectroscopy. Light scattering measurements were carried out on a SEMATech apparatus using laser light with $\lambda = 632.8$ nm in toluene solution with the dn/dc = 0.106. SEC measurements were carried out on a Waters apparatus fitted with ultra styrogel columns (10^3 Å, 10^4 Å, 10^5 Å and 10^6 Å). The elution solvent was THF, with the flow rate of 1.0 mL/min. UV Spectroscopy measure-ments were performed on a Philips PU 8800 UV/vis spectrophotometer apparatus.

RESULTS AND DISCUSSION

The new "in-in" method used in this paper consists of a two-step process. In step 1, a polystyrene star poly-mer with poly (DVB) core was produced using the arm-first method. Characterization on the samples was carried out using SEC, light scattering and visco-metry. Since the hydrodynamic volume of a star polymer is much smaller than a linear sample, with the same molecular weight, therefore, the values of the molecular weight obtained by SEC technique, calibrated with linear samples, is far lower than the real molecular weight of a star polymer.

SEC Apparatus fitted with three detectors in series (low-angle light scattering, photometer and continuous viscometer) is efficient for rapid and proper characterization of star-shaped polymers [23]. In this work, light scattering technique is used for measuring the real weight-average molecular weight ($\overline{M}_w$) of the star samples, and SEC technique is used for determining the polydispersity and the shape of the molecular weight distribution curves. Then by having the weight-average molecular weight and polydispersity of the star samples, the number-average molecular weight of the samples is calculated (PDI = $\overline{M}_w / \overline{M}_n$). The average number of the arms of
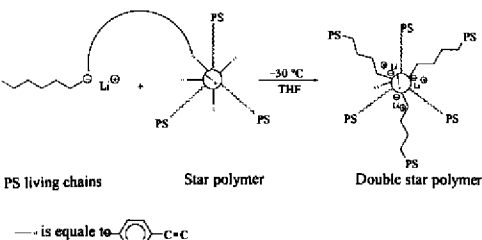
the star polymers is then calculated using the following equation [20,24]:

$$\tilde{f} = \frac{M_{star\,polymer}}{M_{precursor} + M_{DVB}\left(\dfrac{DVB}{Li^+}\right)} \tag{1}$$

Where, f is the average number of the arms, $M_{star\,polymer}$ and $M_{precursor}$ are the number average molecular weight ($\overline{M}_n$) of the star polymer and the initial polystyrene chains, respectively. M_{DVB} is the molecular weight of DVB and (DVB/Li^+) is the mole ratio of DVB to BuLi initiator, which is chosen to be 10 in the experiments. The synthesized polymer sample was precipitated, dried and kept for the next step.

In step 2, first living polystyrene chains were synthesized and a fraction of it was sampled out for characterization. Then, 2 g of the star polymer synthesized and characterized in the previous step was dissolved in THF and added to the system. In order to be sure about the repeatability of the reaction, two different experiments were run in the same condition. The only difference between these two experiments is the allowed stirring time after addition of the star polymer to the system in the second step. This time was set to be 5 and 45 minutes for experiments 1 and 2, respectively.

As it was expected, the living polystyrene chains attacked the double bonds of the cores of the star molecules and attached to them by opening these bonds (Figure 1). Direct evidence of reducing the amount of the double bonds of the cores was obtained by UV spectroscopy on the basis of the work of Rein et al. [19]. These double bonds conjugated with benzene rings exhibit absorption at $\lambda \cong 295$ nm (Figure 2). By measuring the height of the peaks at $\lambda \cong 295$ nm, it is obvious that in experiment 1, during the reaction of the second step, about 60 % of the residual double bonds of the cores are consumed.
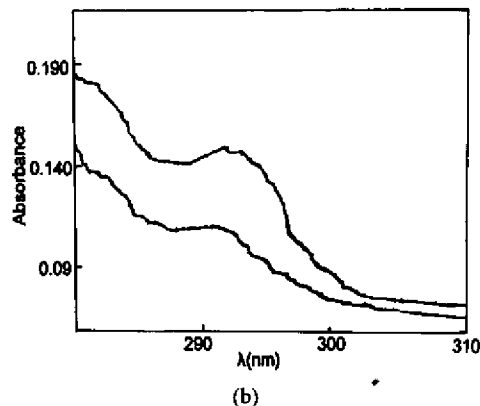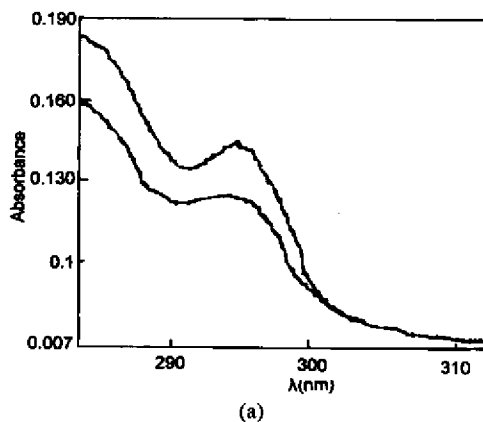
Figure 2. UV Spectroscopy result of the samples: (a) UV Spectroscopy of the star polymer (upper line) and double star (bottom line) for experiment 1, (b) UV Spectroscopy of the star polymer (upper line) and double star (bottom line) for experiment 2.
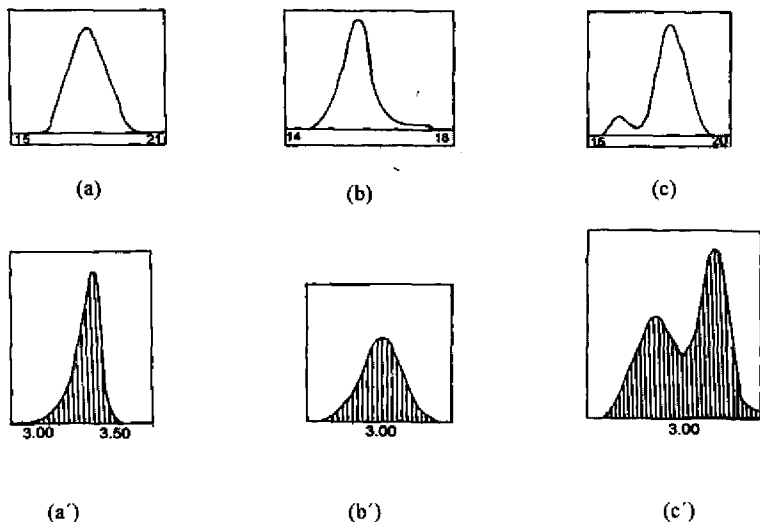

Figure 1: The mechanism of producing double start polymers.

(a)

(b)

(c)

(a´)

(b´)

(c´)

Figure 3. SEC Distribution curves for experiment 1 (a, b, c) and experiment 2 (a´, b´, c´): (a) Living polystyrene synthesized in step 2, (b) star polymer synthesized in step 1, (c) final product at the end of the step 2. (a´) Living polystyrene synthesized in step 2, (b´) star polymer synthesized in step 1, (c´) final product at the end of the step 2 for experiment 1.

But in experiment 2, which has had more stirring time, about 75 % of the residual double bonds are consumed.

After characterization of the products by SEC and LS it was noted that during the reaction of the second step, the molecular weight of the star polymer produced in the first step was increased significantly, which showed the increase of the number of the arms in this polymer.

In the following equation the number of the added arms in the step 2 is determined:

$$f = \frac{M_{double-star} - M_{star-polymer}}{M_{branch}} \qquad (2)$$

In this equation, $M_{double-star}$, $M_{star-polymer}$ and M_{branch} are the number molecular weights ($\overline{M}_n$) of the double-star synthesized in step 2, the star polymer synthesized in the step 1 and the added chains in step 2, respectively.

In Figure 3, the SEC molecular weight distribution curves of the star polymer, the living polystyrene in step 2 and the final product consisting of the double-star polymer for these two experiments are shown.

As it is indicated in Figures 3(C) and (C') (experiment 1 and 2) the molecular weight distribution curves for the final products are bimodal. One of the peaks is related to the double-star polymer synthesized in step 2 and the other one to the unreacted polystyrene chains. It is obvious that in experiment 2, which the system has had more stirring time, the area under the peak of the double-star polymer to that of the unreacted chains is increased significantly.

Other results of these two experiments are shown in Table 1. It should be noted that the relatively large molecular weight distribution of the precursor chains is due to slow initiation of n-BuLi as an initiator for anionic polymerization. As shown in this table, in experiment 1, the number of the arms of the

Table 1. SEC and light scattering results of the samples.

Exp. No.	Polystyrene synthesized in step 1			Star polymer synthesized In step 1			Polystyrene synthesized in step 2			Double star polymer synthesized in step 2		
	$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SEC)	PDI (SEC)	$\bar{M}_w$ (LS)	PDI (SEC)	f (calculated)	$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SEC)	PDI (SEC)	$\bar{M}_w^*$ (LS&calculation)	PDI (SEC)	f* (calculated)
1	7000	11000	1.57	478000	1.80	32	5000	9000	1.74	671000	1.21	111
2	7000	9000	1.27	624000	2.32	32	7000	12000	1.73	1045000	1.7	142

(*) By measuring the weight average molecular weight of the final product with LS and determining the weight ratio in the two peaks of the bimodal distribution curve of SEC and using the equation $M_w = \sum W_i M_i / \sum W_i$, the weight average molecular weight of the double star polymer was calculated. (f)= average number of the arms in the star polymer; (f*)= average number of the arms in double star polymer; (M_n)= number average molecular weight ; (M_w)= weight average molecular weight ; PDI=polydispersity index.

Table 2. Dilute solution properties of the samples.

Exp. No.	Polystyrene synthesized in step 1 (LS)		Star polymer synthesized in step 1(LS)		Double-star polymer synthesized in step 2 (LS & calculation)*	
	Rg (Å)	[η] (mL/g)	Rg (Å)	[η] (mL/g)	Rg (°A)	[η] (mL/g)
1	28.34	9.09	94.14	17.40	101.29	—
2	30.44	7.51	96.10	14.42	106.45	—

*With the help of the weight ratio of two peaks in the bimodal GPC distribution curve of the final product and measuring the radius of gyration (Rg) of the final product by LS and solving these three equations: $Rg_z = \sum x_i \, Rg_i^3 / \sum x_i \, Rg_i^2$, $\bar{M}_w = \sum x_i \, \bar{M}_i^2 / \sum x_i \, \bar{M}_i$, $\bar{M}_w = \sum w_i \, \bar{M}_i / \sum w_i$ together, the mole fraction of the double star polymer (x_i) and its radius of gyration (Rg_i) was calculated.

star polymer was increased from 32 in the first step to 111 in the second step (an increase of 79 arms). However, this increase was about 110 arms (i.e., from 32 to 142 arms) in experiment 2. These results show that the second step of the reaction is diffusion-limited process, due to the existence of the arms surrounding the initial star polymer. This means that the attachment of the living polystyrene chains to the star cores needs sufficient stirring time.

In order to be sure about the number of potential grafting sites of the core of the star polymers, for one of the samples (star polymer synthesized in experiment 1) an exact titration was done with sequential addition of n-BuLi and a 0.1 % solution of methanol in clean benzene [19]. It was found that for neutralization of approximately all the double bonds existing in 9.5×10^{-6} mol of this star polymer, 1.45×10^{-3} mol of n-BuLi is consumed, which means that each star molecule has about 153 unreacted double bonds. As it is mentioned in the previous paragraph, in experiment 1, during the reaction of the second step 79 arms are added to the initial star polymer. It shows that about 52 % of the residual double bonds are consumed. Since there are many error sources in a titration method, so the obtained result is reasonable in accordance with the UV spectroscopy measurements.

In Table 2, some dilute solution properties of the samples are shown. As it is obvious, in both experiments the increase of the radius of gyration of the double-star polymer compared to the initial star polymer, is another reason for the increase of the number of arms during this process.

In this table, there is also the intrinsic viscosity of the star polymer and its precursor chains. Unfortunately, as there were some unreacted chains in the final product, it was not possible to determine the intrinsic viscosity of the double-star polymer indivi-
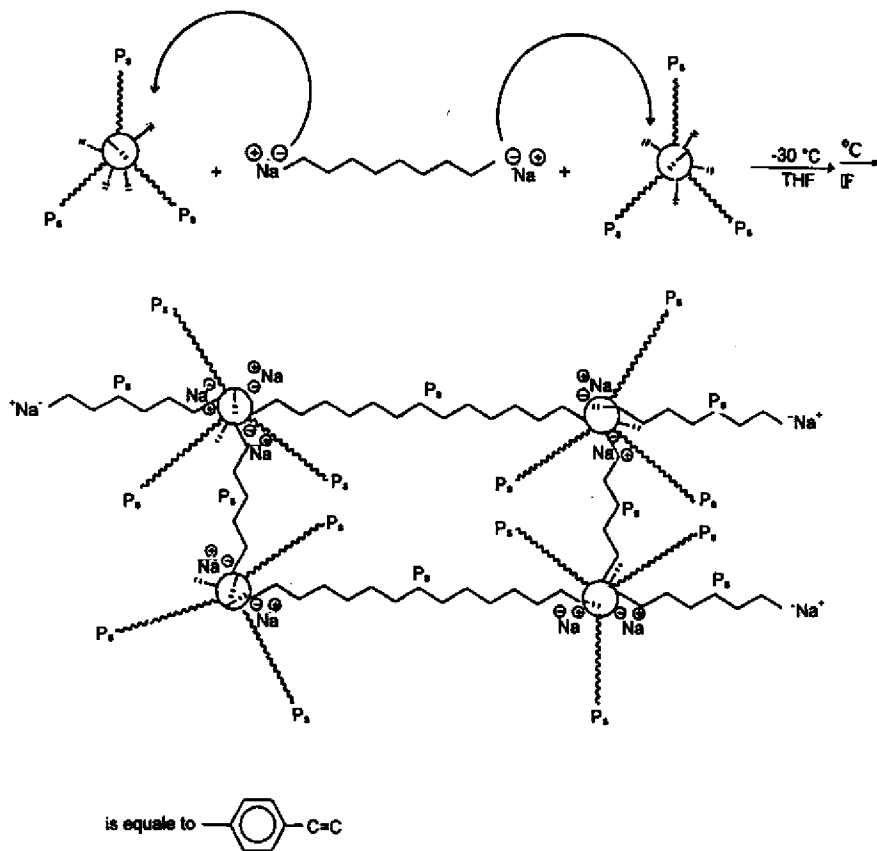
is equale to ——⟨◯⟩—C≡C

Figure 4: The mechanism of gel formation.

dually. But in the case of the star polymers and its precursor chains, synthesized in step 1 the measurements were simply done using Ubbelhode viscometry in toluene at 30 °C.

By using the following equation, the number of arms (f) in a star polymer relates to the ratio of the intrinsic viscosity of the star polymer to that of the arm ($[\eta]_{star} / [\eta]_{arm}$) for $f \geq 6$ in good solvents [25].

$$[\eta]_{star} / [\eta]_{arm} = f^a \{10^{(0.36-0.8 \log f)}\} \qquad (3)$$

Where, α is the exponent in the intrinsic viscosity-

molecular weight relationship of the linear polymer. By considering α = 0.75 in the above equation, the number of arms for the star polymers produced in experiments 1 and 2 are expected to be 36 and 34, respectively, which are very close to the number 32 that was calculated from eqn (1).

To confirm the results of the previous experiments, another experiment was run the same as before but the initiator used in step 2 was sodium naphthalene instead of BuLi. In this case at the beginning of the step 2 bifunctional linear polystyrene chains were synthesized instead of the monofunctional ones. Then

the same as previous experiments, after synthesis of the bifunctional linear polystyrene chains, a known amount of the star polymer made in the first step of experiment 1 was dissolved in THF and added to the system.

It was expected that each end of these bifunctional chains attaches to the cores of different star polymers and gelation occurs (Figure 4). In practice, the formation of an irreversible gel at the end of the experiment confirmed the above expectation.

CONCLUSION

The new "in-in" method used in this work is a two-step process for synthesis of polystyrene double-star polymers without occurrence of any gelation during the reaction. In the first step a star polymer with polystyrene arms and poly (DV B) core is synthesized by an arm-first method and later deactivated, precipitated and dried. In the second step, a known amount of this synthesized and characterized star polymer is dissolved in THF and added to linear living polystyrene chains. The active carbanions at the end of the polystyrene chains attack the double bonds existing in the cores of the star polymers and attach to the star molecules by opening these bonds. Light scattering, SEC and UV spectroscopy results confirm the mentioned reaction and formation of the double-star polymers (i.e., the number of the arms of the star polymer were increased from step 1 to step 2). The number of the added arms was proportional to the allowed mixing time, after addition of the star polymer to the system in the second step.

Finally, to prove the above results, in another experiment with similar manner, bifunctional polystyrene chains were used in step 2 instead of the monofunctional ones. As it was expected, each end of the bifunctional chains attaches to the cores of different star polymer and an irreversible gel was formed. It should be noted that an important characteristic of the gels made by "in-in" method, is that the chain length between the nodes is well defined and can be adjusted arbitrarily.

It seems that, with the monomers, which are able to attack the double bonds existing in the core of the star polymers, it is possible to synthesize hetero-arm star polymers by this new method. However, it should be mentioned that, in this new method, the outer ends of the arms are not active. Hence, if the aim of the synthesis of the star polymer is to functionalize the outer end of the arms or to carry out other reactions, this method may not be feasible.

ACKNOWLEDGEMENTS

REFERENCES

1. Morton M., Helminiak T. E., Gadkary S. D. and Bueche F., "Preparation and properties of monodisperse branched polystyrene", *J. Polym. Sci.*, **57**, 471 (1962).

2. Roovers J., Hadjichristidis N. and Fetters L. y., "Analysis and dilute solution properties of 12 and 18-arm-star polystyrene", *Macromolecules*, **16**, 214 (1983).

3. Iatrou H. and Hadjichristidis N., "Synthesis of a model 3-Mikto arm star terpolymer", *Macromolecules*, **25**, 4649 (1992).

4. Allgaier J., Young R.N., Efstratiadis V. and Hadjichristidis N., "Synthesis and characterization of PI/PS A_2B_2 star copolymers", *Macromolecules*, **29**, 1794 (1996).

5. Zilliox J. G., Rempp P. and Parrod J., "Preparation de macromolecules a structure en etoile, par copolymerization anionique", *J. Polym. Sci. C*, **22**, 145 (1968).

6. Young R. N. and Fetters L. J., "Star-branched polymers. The reaction of dienyllithium chains with the isomers of DVB", Macromolecules, **11**, 899 (1978).

7. Eschwey H. and Burchard W., "Star polymers from styrene and DVB", *Polymer J.*, **16**, 180 (1975).

8. Masuda T., Ohta Y., Yamauchi T. and Onogi S., "Characterization and rheological properties of multi-branched star PS", *Polymer J.*, **16**, 3, 273 (1984).

9. Afshar Taromi F. and Rempp P., "Porcupine polymers and double-star polymers", *Makromol. Chem.*, **190**, 1791 (1989).

www.SID.ir

10. Bi L. K. and Fetters J., "Domain morphology of star block copolymers of PS and PI", *Macromolecules*, **8**, 90 (1975).

11. Bi L. K. and Fetters J., "Synthesis and properties of block copolymers. PS-Polydiene star block copolymers", *Macromolecules*, **9**, 5, 732 (1976).

12. Lutz P. and Rempp P., "New developments in star polymer synthesis", *Makromol. Chem.*, **189**, 1051 (1988).

13. Gnanou Y., Lutz P. and Rempp P., "Synthesis of star-shaped PEO", *Makromol. Chem.*, **189**, 2885 (1988).

14. Rein D., Lamps J.P., Rempp P., Lutz P., Papanagopoulos D. and Tsitsilianis C., "New developments in synthesis of star polymers with PEO arms", *Acta Polymer*, **44**, 225 (1993).

15. Buchholz U., Lutz P., Kunz M. and Burchard W., "Electron microscopy on highly branched PS star-shaped polymers", *Makromol. Chem.*, **194**, 1371 (1993).

16. Okay O. and Funke W., "Steric stabilization of reactive microgels from 1,4-DVB", *Makromol. Chem., Rapid Commun.*, **11**, 583 (1990).

17. Tsitsilianis C., Graff S. and Rempp P., "Hetero-arm star copolymers with potentially ionogenic branches", *Eur. Polym. J.*, **27**, 243 (1991).

18. Rein D. H., Rempp P. and Lutz P. J., "Kinetics of arm-first star polymers formation in a non-polar solvent", *Makromol. Chem. Phys.*, **199**, 569 (1998).

19. Tsitsilianis C., Papanagopoulos D. and lutz P., "Amphiphilic hetero-arm star copolymers of PS and PEO", *Polymer*, **36**, 19, 3745 (1995).

20. Tsitsilianis C., Chaumont P. and Rempp P., "Synthesis and characterization of hetero-arm star copolymers", *Makromol. Chem.*, **191**, 2319 (1990).

21. Tsitsilianis C. and Voulgaris D., "Poly(2- vinyl pyridine) based star-shaped polymers", *Makromol. Chem. Phys.*, **198**, 997 (1997).

22. Afshar Taromi F., Gallot Z. and Rempp P., "Characterization of star-shaped PS samples by SEC", *Eur. Polym. J.*, **25**, 1183 (1989).

23. Storey R. F., Shoemake K. A. and Chisholm B. J., "Synthesis and characterization of multi-arm star-branched polyisobutylenes", *J. Polym. Sci., Part A, Polym. Chem.*, **34**, 2003 (1996).

24. Mishra M. K. and Kobayashi Sh., *Star and Hyperbranched Polymers*, Marcel Dekker , New York, Ch. 2, 28–51, Ch. 11, 308–315 (1999).