One-Step Synthesis of Star-Block Copolymers via Simultaneous Free Radical Polymerization of Styrene and Ring Opening Polymerization of epsilon-Caprolacton Using Tetrafunctional Ini...

2 AUTHORS, INCLUDING:

Ismail Cakmak
Kafkas University
32 PUBLICATIONS   **259** CITATIONS

One-Step Synthesis of Star-Block Copolymers via Simultaneous Free Radical Polymerization of Styrene and Ring Opening Polymerization of ε-Caprolacton Using Tetrafunctional Iniferter

Temel Ozturk, Ismail Cakmak

Department of Chemistry, Kafkas University, Kars 36200, Turkey

ABSTRACT: Star-block copolymers comprised of poly (styrene) (S) core and four poly(ε-caprolacton) (ε-CL) arms were synthesized by the combination of free radical polymerization (FRP) of S and ring opening polymerization (ROP) of ε-CL in one-step in the presence of tetrafunctional iniferter. The block copolymers were characterized by ^{1}H-NMR and FTIR spectroscopy, gel permeation chromatography (GPC), and fractional precipitation method. ^{1}H -NMR and FTIR spectroscopy and GPC studies of the obtained polymers indicate that star-block copolymers easily formed as result of combination FRP and ROP in one-step. The γ values (solvent/precipitant volume ratio) were observed between 1.04–2.72 (mL/mL) from fractional measurements. The results show that when the initial S feed increased, the molecular weights of the star-block copolymers also increased and the polydispersities of the polymers decreased. M_w/M_n values of the products were measured between 1.4 and 2.86 from GPC. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3277–3281, 2010

Key words: star-block copolymers; ε-caprolacton; iniferter; styrene; ring opening polymerization; one-step

INTRODUCTION

Block copolymers have been extensively studied and have industrial applications in many fields such as adhesives, surfactants, and compatibilization agents in polymer blends. The different techniques of the synthesis of block copolymers are reviewed by several authors.[1–6] In generally, in the synthesis of block copolymers, combination of polymerization types such as anion to radical,[7,8] cation to radical,[9] and anionic to cationic transformations[10] have been used. This route involves transformation reactions in which the mode of propogation of the first monomer is transformed into a different mode suited for the polymerization of the second monomer.[11] These procedures were usually performed in two steps. The synthesis of block copolymers with different techniques in one step has advantages over other methods. Because of applicability of atleast two transformation steps simultaneously, side reactions that lead to homopolymer formation are minimized.

Iniferters are initiators that induce radical polymerization that proceeds via initiation, propagation, primary radical termination, and transfer to initiator.

As Otsu and Yoshida proposed the iniferter concept and discovered the living radical polymerization of vinyl monomers in homogeneous systems, many photoiniferters and thermal iniferters have been prepared and used for vinyl monomer polymerizations to efficiently synthesize polymers with well-defined structures (e.g., block, graft, star, and telechelic polymers); there are many review articles.[12–14]

In recent years, beside these various synthetic methods, one-step process have been sucessfully used for the synthesis block copolymers. Mecerreyes et al.[15] proposed a new strategy for the one-step synthesis of block copolymers involves the use of asymetric difunctional initiator that is able to initiate the simultaneous polymerization of two monomers by different polymerization methods in such a way that this initiator remains attached to each type of growing chain. Aida and Takeuchi[16] studied the one-pot synthesis of the poly(oxetane-b-ε-caprolacton) block copolymer via sequential cationic and anionic polymerizations of oxetane and ε-caprolacton (ε-CL) using triftalate complexes of sterically hindered titanium bisphenolates. Chang and coworkers[17] proposed a new strategy for the one-step synthesis of block copolymers by using a combination of reverse atom transfer radical polymerization (reverse ATRP) and ring opening polymerization (ROP). Poly(styrene-b-ε-caprolacton)/ silicate nanocomposites were prepared via one-pot,
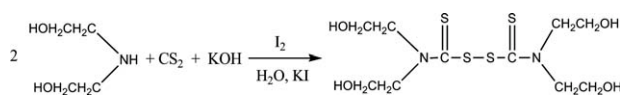

Scheme 1 The synthesis of initiator.

one-step *in situ* living polymerization from a silicate-anchored bifunctional initiator.[18] Poly(styrene-r-maleic anhydride)-b-poly(styrene) block copolymer was synthesized by the controlled radical polymerization of 9 : 1 mixture of styrene and maleic anhydride at 120°C in the presence of 2,2,6,6-tetramethyl-piperidinyloxy as the initiator.[19] Synthetic parameters for the chemoenzymatic cascade synthesis of block copolymers combining enzymatic ROP and ATRP in one-pot were investigated by Heise and coworkers.[20] One-pot polymerization of hexylisocyanate with styrene (S) was investigated using different alkali metal counterions such as Li⁺, Na⁺, and K⁺ with naphtalene in the presence of NaBPh₄ to give the rod-coil-rod triblock copolymer.[21] Well-defined block copolymers were obtained from 4-hydroxy-butyl-2-bromoisobutyrate dual initiator, combining ATRP of *t*-butylmethacrylate and ROP of ε-CL in a one-step process.[22] Amphiphilic poly(styrene-b-*N*-isopropylacrylamide) was prepared by a one-step interfacial-initiated microemulsion polymerization.[23] Star and branched polymers have received much attention because these dense, branched polymers are expected to have different physical properties compared with their linear analogs.[24]

In this article, we report the one-step synthesis of a star-block copolymers by using a tetra functional initiator able to initiate polymerization of ε-CL and S.

EXPERIMENTAL

Materials

Dibutyltin dilaurate (DBTDL) (Merck) was used as supplied. Styrene (99% Aldrich) and ε-CL
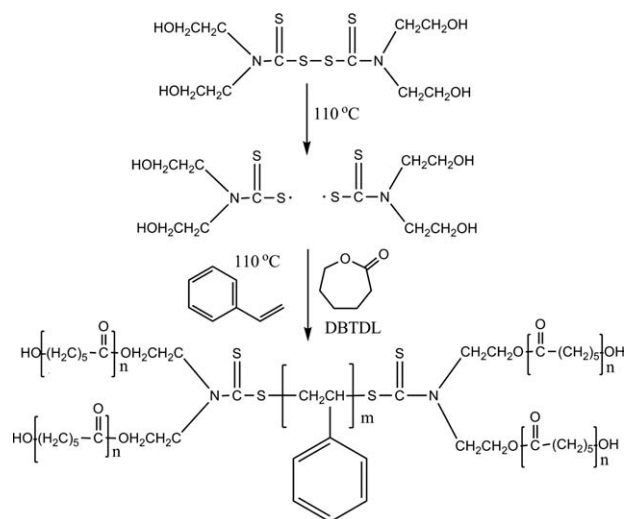
Scheme 2 One-step synthesis of PS-PCL star-block copolymer.

(98% Merck) were purified by conventional methods. All other reagents were purchased from Aldrich or Fluka and used without further purification. *N,N'*-tetra(2-hydoxythyl thiuram disulfide) (HETD) was synthesized by the reaction of diethanol amine, CS₂, and I₂ according to the method reported in the literature,[25] as shown in scheme 1. IR (cm⁻¹): 3357 (—OH), 2923 (—CH2), 1325 (CS—N), 1720 (—C=S). ¹H-NMR (ppm): 4.72 (—NCH₂CH₂O*H*), 2.84–2.97 (—NC*H₂*CH₂OH), 3.40–3.47 (—CH₂C*H₂*OH).

One-step polymerization

The general procedure for one-step polymerization of S and ε-CL is as follows: to a sclenck tube equipped with magnetic stirring bar, initiator, degassed monomers (S and ε-CL), and DBTDL were added. The tube was then degassed by flushing pure argon and placed in a thermostated silicon-oil bath at given temperature. Star copolymers formed were precipitated in 10-fold excess methanol.

TABLE I
The Effect of the Amount of Styrene One-Step Radical Polymerization of Styrene and ε-caprolactone with HETD at 110°C

Code	ε-CL (g)	S (g)	Yield (g)	$\overline{M}_n$, GPC	$\overline{M}_w/\overline{M}_n$	γ[a]	$DP_{n(PS)}$ /$DP_{n(PCL)}$
AE-1	1.0079	0.5029	0.0226	26,149	2.86	1.08	12.1
AE-2	1.0301	0.7507	0.1442	38,007	2.15	1.88	7.9
AE-3	1.0589	1.0073	0.2826	42,296	2.11	2.72	78.3
AE-4	1.2679	1.2555	0.3599	62,770	1.75	1.90	16.0
AE-5	1.0009	1.5174	0.4187	65,944	1.65	1.96	6.5
AE-6	1.0107	2.0059	0.7930	81,446	1.67	1.80	–

HETD = 1.10⁻⁵ mol (3.60 × 10⁻³ g), DTDL = 1.10⁻⁶ mol (6.32.10⁻⁴ g), S/HETD (mol/mol) = 1000/1, Time = 12 h.
[a] Nonsolvent (Petroleum ether, mL)/solvent (THF, mL) γ values of PS and PCL were found as 2.5−3.2 and 3.4−3.6, respectively.

TABLE II
The Effect of the Initiator One-Step Radical Polymerization of Styrene and ε-caprolactone with HETD at 110°C

Code	S/HETD (mol/mol)	HETD (g)	ε–CL (g)	S (g)	Yield (g)	$\overline{M}_n$, GPC	$\overline{M}_w/\overline{M}_n$	γ^a	$DP_{n(PS)}/DP_{n(CL)}$
AD-5	100/1	3.60×10^{-2}	1.5536	1.0267	0.0250	39,161	2.19	2.62	4.32
AD-4	200/1	1.80×10^{-2}	1.5276	1.0212	0.1140	93,836	1.50	1.96	–
AD-3	400/1	9.00×10^{-3}	1.5896	1.0179	0.1270	1,22,339	1.39	1.98	59.0
AD-2	600/1	5.76×10^{-3}	1.5806	1.0043	0.2223	1,04,458	1.49	1.90	–
AD-1	800/1	4.32×10^{-3}	1.5259	1.0424	0.3832	65,410	1.67	1.04	17.6

DTDL = 1.10^{-6} mol (6.32×10^{-4} g), Time = 24 h.
[a] Nonsolvent (Petroleum ether, mL)/solvent (THF, mL) γ values of PS and PCL were found as 2.5–3.2 and 3.4–3.6, respectively.

Characterization of the polymers

The number average molecular weight (M_n) and polydispersities (M_w/M_n) of obtained polymers were measured by gel permeation chromatography (GPC). GPC was performed with a Waters 2414 refractive index detector and Waters model 1515 isocratic pump at a flow rate of 1 mL/min through a combination of Waters HR3, HR4E, and HR4 styragel columns. Poly(styrene) (Shodex SM-105) standards were used to calibrate the columns. The analysis was undertaken at 40°C with HPLC grade THF as an eluent. Waters Breeze software was used for data analysis. The ^{1}H-NMR spectra of the products were obtained from CDCl$_3$ solution on a Bruker NMR Spectrometry. IR spectra were recorded with polymer films cast from benzene solution with a Perkin Elmer 1600 spectrometer. Star-block copolymers were also characterized by fractional precipitation to seperate their homopolymers as reported method in the literature.[26] Fractional precipitation was carried out as follows: Star-block copolymer was dissolved in THF(solvent); and aliquot samples of the solution were taken for the precipitation by adding different volumes of petroleum ether(nonsolvent).

RESULTS AND DISCUSSION

Synthesis of iniferter

The tetrafunctional iniferter was prepared according to the reaction sequence shown in Scheme 1 as described in the literature,[25] and was characterized by ^{1}H-NMR and IR measurement.

One-step block copolymerization

HETD (iniferter) possessing four hydroxyl functions and thiuram disulfide group initiates the ROP of ε-CL and FRP of S simultaneously. A monomer mixture of S and ε-CL that is initiated by the tetra functional initiator in the presence of DBTDL as the ring opening catalyst gives the star-block copolymer. Taking into account that iniferter with four functional groups and termination of S, the obtained polymers should have the structure as depicted in Scheme 2.

Tables I–III give the results from several polymerizations using HETD as initiator. The effect of the the amount of S on one-step block copolymerization is gathered in Table I. The increasing amount of S caused an expected increase in the yield and molecular weights of the star-block copolymers. The

TABLE III
Free Radical Polymerization of Styrene and ε-caprolactone with HETD at 110°C

Code	Time (h)	ε-CL (g)	S (g)	Yield (g)	$\overline{M}_n$, GPC	$\overline{M}_w/\overline{M}_n$	γ^a	$DP_{n(PS)}/DP_{n(CL)}$
AB-1	4	1.5013	1.0035	0.0803	15,574	4.29	2.02	7.48
AB-2	6	1.5184	1.0070	0.0959	17,141	1.89	1.98	38.0
AB-3	8	1.5130	1.0099	0.1333	20,706	1.78	2.02	39.6
AB-4	10	1.5098	1.0072	0.2543	22,624	1.75	2.42	12.4
AB-5	12	1.5066	1.0016	0.3240	31,691	1.65	1.98	5.5
AB-6	15	1.5187	1.0087	0.3582	41,361	1.65	1.96	8.4
AB-7	21	1.6419	1.0098	0.7352	1,18,049	1.43	1.40	0.6
AB-8	27	1.5001	1.0359	0.7775	1,20,048	1.43	1.44	1.0

HETD = 1.00×10^{-5} mol (3.60×10^{-3} g), DTDL = 1.00×10^{-6} mol (6.32×10^{-4} g), S/HETD (mol/mol) = 1000/1.
[a] Nonsolvent (Petroleum ether, mL)/solvent (THF, mL) γ values of PS and PCL were found as 2.5–3.2 and 3.4–3.6, respectively.
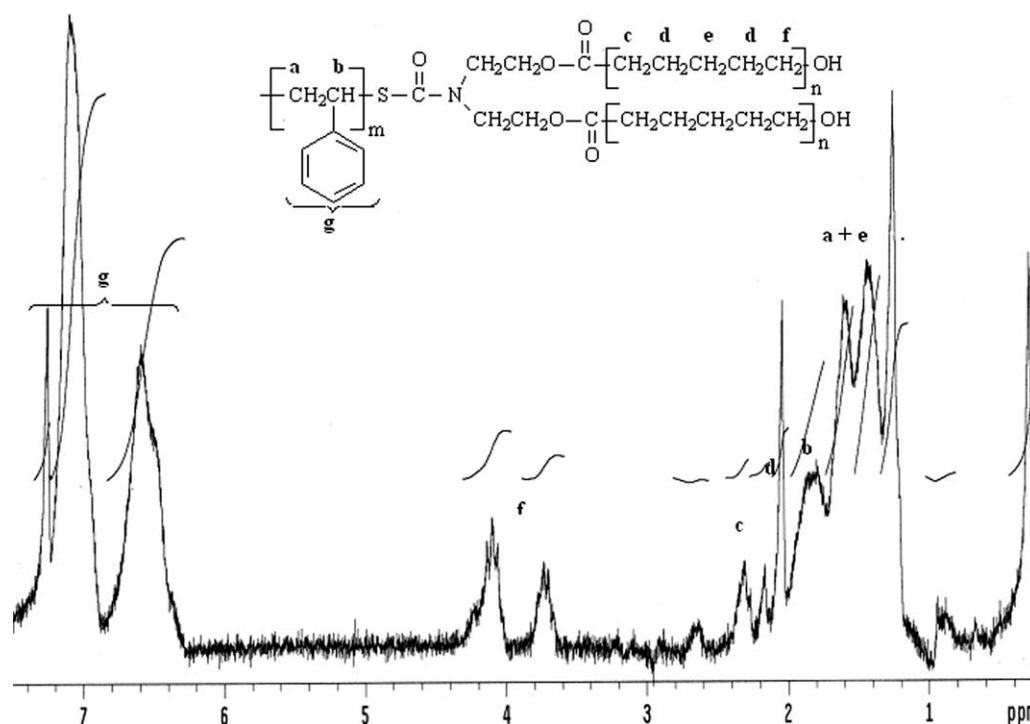
Figure 1 ^{1}H-NMR spectrum of PS-PCL star-block copolymer (Code: AD-3 in Table I).

increased amount of iniferter (HETD) in the reaction mixture leads to the formation of higher number of active centers. For this reason, more growing macro radicals are formed in the system, but they have shorter PS segments, which is confirmed by a decrease in molecular weights and an increase in

polydispersities (1.67–2.19) of the star-block copolymers (Table II). As can be seen, M_n of the star-block copolymers (Table III) increased linearly with the polymerization time, which indicates that this polymerization proceeds via quasi-living radical mechanism in manner proposed by Otsu et al.[27]
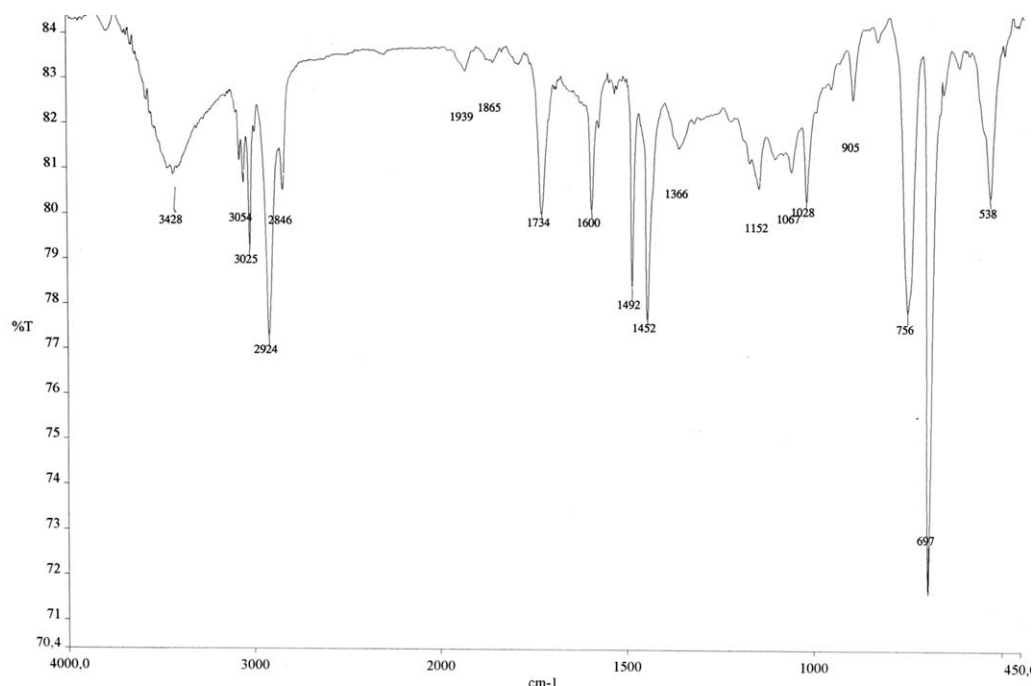

Figure 2 FTIR spectrum of PS-PCL star-block copolymer (Code: AD-3 in Table I).

Fractional precipitation experiments provide definite evidence for the formation of block or graft copolymer. The gamma-values of the products are different from their related homopolymers, as shown Tables I, II, and III.

Characterization of star-block copolymers

A series of star-block copolymers with poly(ε-caprolacton) (PCL) and PS blocks of various molecular weights were synthesized by the combination of FRP and ROP in one-step in the presence of HETD with DBTDL as a catalyst. Star-block copolymers were characterized by ^{1}H-NMR, FTIR, and GPC measurements. Figure 1 shows the ^{1}H-NMR spectrum of the star-block copolymer. The triplet peak at 4.07–4.25 ppm can be attributed to the $-CH_2OH$ protons of the PCL unit; the other three signals at 2.66, 2.28, and 1.44 ppm can be assigned to the methylene protons of the PCL blocks as marked in Figure 1. The ^{1}H-NMR spectrum of PCL-PS star-block copolymer in Figure 1 shows characteristic signals at 7.26, 7.08, and 6.60 ppm aromatic protons of PS chain. The FTIR spectrum of the star-block copolymer is shown in Figure 2. Each spectrum has the characteristic $-OH$ group, aromatic $-C-H$, aliphatic $-CH$, aromatic overtone, $-C=O$, phenyl $-C-H$ and $-C-O$ (ether linkage) bands at 3428, 3054, 3025, 2924, 1939, 1734, 1600, and 1152 cm^{-1}, respectively. Homopolymer of PS and PCL were separated at different volume ratios to solvent(γ). γ values of PS and PCL were found as 2.5–3.2 and 3.4–3.6 respectively. The degree of polymerization ratios $(DP)_{PS}/(DP)_{CL}$ (m/n) were determined by comparing the integrated intensities of benzylic protons of PS chain at 6.6–7.2 ppm to $-CH_2$ protons of PCL chains at 2.3 ppm.

CONCLUSION

An iniferter possessing thiuram disulfide and hydoxy functions have been prepared by the reaction of diethanol amine, CS_2, KOH and iodine. The iniferter can be used by the combination of FRP of S and ROP ε-CL in one-step to obtain PCL-PS star-block copolymers. The proposed procedure for the preparation of star-block copolymers are simple and efficient.

References

1. Hazer, B. Handbook of Polymer Science and Technology; Cheremisnoff, N. P., Ed.; Dekker: New York, 1989; Vol. 1, p 133.
2. Abadie, M.; Ourahmonue, D. Br Polym J 1987, 14, 247.
3. Nuyken, O.; Weidner, R. Adv Polym Sci 1988, 73, 1471.
4. Jerome, R.; Tayt, T.; Quhadi, T. Prog Polym Sci 1984, 10, 87.
5. Cakmak, I. Macromol Rep 1995, 32, 197.
6. Cakmak, I. Macromol Rep 1995, 32, 1113.
7. Vinchon, Y.; Reeb, R.; Riess, G. Eur Polym J 1976, 12, 317.
8. Hazer, B.; Cakmak, I.; Kucukyavuz, S.; Nugay, T. Eur Polym J 1992, 28, 1295.
9. Haese, F. D.; Goethals, E. J.; Tezuka, Y.; Imai, K. Makromol Chem Rapid Commun 1986, 15, 293.
10. Burgess, F. J.; Cunliffe, A. V.; Maccallum, J. R.; Richards, D. H. Polymer 1977, 18, 726.
11. Yagci, Y.; Mishra, M. K. Macromolecular Design: Concept and Practice; Mishra, M. K., Ed.; Polymer Frontiers Int.: Hopewell Jct, NY, 1994; p 391.
12. Otsu, T.; Matsumoto, A. Macromolecular Design: Concespts and Practice, Mishra, M. K., Ed.; Polymer Frontiers Int.: New York, 1994; Chapter 12, p 481.
13. Otsu, T.; Matsunaga, T.; Doi, T.; Matsumoto, A. Eur Polym J 1995, 31, 67.
14. Otsu, T.; Matsumoto, A. Adv Polym Sci 1988, 136, 75.
15. Mecerreyes, D.; Moineau, G.; Dubois, P.; Jerome, R.; Hedrick, J. L.; Hawker, C. J.; Malstrom, E. E.; Trolsas, M. Angew Chem Int Ed 1998, 37, 1724.
16. Takeuchi, D.; Aida, T. Macromolecules 2000, 33, 4607.
17. Huang, C. F.; Kuo, S. W.; Lee, H. F.; Chang, F. C. Polymer 2005, 46, 1561.
18. Sogah, D. Y.; Di, J. Macromolecules 2006, 39, 5052.
19. Benoit, D.; Hawker, C. J.; Huang, E. E.; Lin, Z.; Russel, T. P. Macromolecules 2000, 33, 1505.
20. Geus, M. D.; Schormans, L.; Palmans, A. R. A.; Koning, C. E.; Heise, A. J Polym Sci Part A: Polym Chem 2006, 44, 4290.
21. Hwan, J.; Lee, J. S. Macromol Rapid Commun 2003, 24, 571.
22. Eddine, M. N.; Delatie, C.; Hurtrez, G.; Dumas, P. Eur Polym J 2005, 41, 313.
23. Zhen, C.; He, W. D.; Liu, W. J.; Li, J.; Li, J. F. Macromol Rapid Commun 2006, 27, 1229.
24. An, S. G.; Li, G. H.; Cho, C. G. Polymer 2006, 47, 4154.
25. Nair, C. P. R.; Clouet, G.; Chaumont, P. J Polym Sci Part A: Polym Chem 1989, 27, 1795.
26. Hazer, B.; Baysal, B. M. Polymer 1986, 27, 961.
27. Otsu, T.; Yamashita, K.; Tsuda, K. Macromolecules 1986, 19, 287.