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Synthesis of poly[ε-caprolacton-b-epichlorohydryin-b-ε-caprolactone]-g-poly(styrene) Block-Graft Copolymers via Cationic Ring Opening and Atom Transfer Radical Polymerization Transformations

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ABSTRACT: The poly[(ε-caprolacton-b-epichlorohydrin-b-ε-caprolactone)]-g-(polystyrene-) [(PCL-b-ECH-b-PCL)]-g-PS block-graft copolymers were prepared via cationic, ring opening (ROP) and atom transfer radical polymerization (ATRP) transformations. With this goal in the first, cationic ring-opening technique was used to polymerize the epichlorohydrin (ECH). The ring opening polymerisation (ROP) of ε-caprolactone (ε-CL) was carried out using poly (epichlorohydrin) (PECH) with hydroxyl functional groups acting as initiators at 110 ºC to yield poly(ε-caprolacton-b-epichlorohydrin-b-ε-caprolactone) (PCL-PECH-PCL) block copolymer. Finally, in the atom transfer radical polymerisation (ATRP) of the styrene, chloromethyl groups of the PECH segment of PCL-PECH-PCL were used as the starting functional group. [PCL-b-PECH-b-CL] -g-PS graft copolymer block was obtained as a result of polymerization. The results of the analysis indicated that the molecular weights of the graft copolymers increased linearly with styrene polymerisation. Synthesized polymers were characterized by ^{1} H-NMR, GPC and DSC techniques.

Keywords: ATRP, ROP, block copolymer, block-graft copolymer, epichlorohydrin, ε-caprolacton.

Poli - [(ε-kaprolakton-b-epiklorohidrin-b-ε-kaprolakton)] - g- (polistiren-) [(PCL-b-ECH-b-PCL)] - g-PS Blok-aşı Kopolimerleri Katyonik, Halka Açıklma Polimerizasyonu (ROP) ve Atom Transfer Radikal Polimerizasyon (ATRP) Tekniklerinin Kombinasyonu ile Sentezi

ÖZET: Poli - [(ε-kaprolakton-b-epiklorohidrin-b-ε-kaprolakton)] - g- (polistiren -) [(PCL-b-ECH-b-PCL)] - g-PS blok-aşı kopolimerleri katyonik, halka açıklama polimerizasyonu (ROP) ve atom transfer radikal polimerizasyon (ATRP) tekniklerinin kombinasyonu ile sentezlenmiştir. Bu amaçla, epiklorohidrin (ECH) polimerize etmek için katyonik halka açma tekniği kullanılmıştır. Sentezlenen, Hidroksil fonksiyonel gruplu poli (epiklorohidrin) (PECH), ε-kaprolaktonun (ε-CL) 110 ° C'de halkalı açılma polimerizasyonunun (ROP) başlatıcısı olarak poli (ε-kaprolakton-b-epiklorohidrin- B-ε-kaprolakton) (PCL-PECH-PCL) blok kopolimerinin eldesinde kullanıldı. Son olarak, başlatıcı olarak PCL-PECH-PCL'nin PECH bloğunun klorometil gruplarını kullanarak gerçekleştirilen stirenin atom transfer radikal polimerizasyonu (ATRP), [PCL-b-PECH-b-CL] -g-PS-graft kopolimeri oluşumuyla sonuçlanmıştır. Elde edilen sonuçlar, graft kopolimerlerinin moleküler ağırlıklarının stiren dönüşümüyle arttığını gösterdi. Polimerler, ^{1}H-NMR, GPC ve DSC teknikleri ile karakterize edildi.

Anahtar Kelimeler: ATRP, ROP, blok kopolimer, blok-aşı kopolimer, epiklorohidrin, ε-kaprolakton.

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INTRODUCTION

Numerous monomers have been polymerized by this technique after Matyjaszewski (Wang et al., 1995a) reported the ATRP technique, which uses compounds of alkyl halides as initiators and a Cu (I) -ligand complex as a catalyst. (Kato et al., 1995; Percec et al., 1995; Muftuoglu et al., 2004; Coessens et al., 2001). ATRP is one of the most suitable controlled polymerization technique to polymerize styrene and acrylate derivatives, and a range of other monomers yielding polymers with low polydispersities (PD)(Okcu et al., 2010; Du et al., 2015). Comparing to the other living/controlled radical polymerizations techniques, the ATRP has drawn widespread attention because of its many advantages and great industrialization prospects (Wang et al., 1995b). ATRP method has served a very important purpose for the preparation of new different type functional copolymers with controlled molecular weights and low polydispersities(PDI) (Matyjaszewski 1998; Chen et al., 2015).

The complexes of transition metals like Cu(I), Ni(II), Ru(II), Fe(II) and Os(II) have been used as catalysts in ATRP for the preparation of block copolymers (Matyjaszewski 1998; Braunecker et al., 2007). Copper (II) based catalysts are the most convenient and cheapest in terms of cost as well. Copper(I)-catalyzed ATRP is one of the most important techniques for controlling radical polymerizations (Matyjaszewski 1998; Tsarevsky et al., 2006).

There are many attempts to prepare block and graft copolymers due to their various properties and applications (Alam et al., 2015; Cakmak et al., 2006; Cakmak et al., 2008; Szabó et al., 2015). One of those polymers called segmented copolymers have some advantages like incorporated at least two or more polymer blocks possesing different chemical properties into one polymer segment. A wide range of disjointed copolymer properties can be prepared and inserted into the copolymers by using different monomers (Okrasa et al., 2004). The most suitable materials for the different applications are the polymers contain a specific combination of block and graft copolymers (Stoeckel et al., 2002).

Ring-opening polymerization (ROP) is a very useful polymerization technique for controlled synthesis of aliphatic polyesters (Stridsberg et al., 2002; Yuan et al., 2008; Yang et al., 2008; Erdogan et al., 2005) such as polylactide, polyglycolide, polymandelide, polyvalerolactone, or poly(ε-caprolactone) (PCL). Cakmak et al. prepared PECH-PS, PECH-PMMA graft copolymers by the transformation of cationic, photopolymerization and ATRP process (Cakmak and Baykara, 2006; Cakmak et al., 2008). Preparation of PECH-b-St-gPMMA block-graft copolymers by the transformation of activated monomer, nitroxide mediated polymerization and ATRP techniques was described by Yagci et al.(Tasdelen et al., 2007). Cho was synthesized various cyclic monomers having -CN, $-CO_2R$ and $-C_6H_5$ groups and these monomers were polymerized via radical ring-opening mechanism to obtain high molecular weight polymers (Cho, 2000). Yao et al. prepared and characterized a sequence of new anilido-imine-Al complexes, and those complexes were used as initiators for the polymerization of 3-caprolactone via ring opening mechanism(Yao et al., 2008).

Chen et al. synthesized and characterized Fe(II)/heterocyclic carbene coordination compounds. These complexes were used for polymerization of ε-caprolactone via ring opening mechanism as a single component initiator (Chen et al., 2006). Messman et al. carried out the ring-opening polymerization (ROP) of L-lactide, used Poly(L-lactide) in ATRP to yield molecular wight contollable linear block copolymers (Messman et al., 2005). Gowda et al used $FeCl_3·6H_2O$, $RuCl_3·H_2O$ and $FeCl_2·4H_2O$ catalysts for polymerization of ε-caprolactone, δ-valerolactone and β-butyrolactone by ring opening method(Gowda and Chakraborty, 2009).

In this reasearch, we present the preparation and characterization of ABA block copolymer chains of poly(epichlorohydrin) (PECH) (A block) and mediated PCL (B block) using ROP. Then, using this poly(ε-caprolacton-b-epichlorohydrin-b-ε-caprolactone) [poly(ε-CL-b-ECH-b-ε-CL)] block copolymers, poly(ε-caprolacton-b-epichlorohydryn-g-polystyreneb-ε-caprolactone) [poly(ε-CL-b-ECH-g-PS-b-ε-CL)] block-graft copolymers were synthesized by ATRP. The bulk-ATRP of Styrene (S) was carried out using CuCl/2,2'-bipyridine (bpy) complex as catalyst.

MATERIALS AND METHODS

Cupper (I) chloride (CuCl), ε-caprolactone (ε-CL), epichlorohydrin (ECH), stannous octoate (Sn(oct)$_2$) and 2,2'-bipyridine (bpy) were supplied from Merck or Aldrich. The styrene was obtained from Merck Company and the extraction was carried out with 10% NaOH solution and purified by conventional procedure. The other materials were supplied from Aldrich or Fluka and used as purchased.

Cationic Polymerization of ECH: 30 ml of CH 2 Cl 2 and 10 g of 57% HBF 4 were added to a flask and a magnetic stirrer was used for homogeneous mixing. The reaction was set so that nitrogen gas would pass through it. To the reaction vessel, 96 g of epichlorohydrin were added(3 hour periods).

The reaction contents were poured into 1 L of water to remove inorganic impurities and the organic phase was separated. After drying with MgSO4 and evaporation of the organic phase, a viscous substance remained in the glass vessel. (23.0 g 36 % yield of ECH). M_n: 1611 g/mol M_w/M_n: 1.04, ^{1}H-NMR (ppm): 4.02-4.10 (HOC$\underline{H}_2$), 3.69-3.60 (C$\underline{H}$O) , 3.97-3.83 (OC$\underline{H}_2$Cl).

Ring-opening Polymerization of ε-CL: The general recipe for ROP of ε-CL with PECH as follows: to a Schlenck tube containing magnetic stirring bar, macroinitiator (PECH) and monomers with bulbed by nitrogen (ε-CL) were added.

The tube content were degassed by bulbing pure nitrogen again and placed in a termostated silicon-oil bath at 110 ^{o}C. PCL-PECH-PCL block copolymers synthesized were precipitated in excess methanol to remove unreacted ε-caprolactone and the soluble small impurities. The synthesis conditions and the results can be seen in Table 1.

Table 1. ROP of ε-CL with PECH at 110°C

Code	Time (h)	ε-CL (g)	PECH (g)	Yield of polymer (%)	$\overline{M}_{n\,GPC}$	$\overline{M}_w/\overline{M}_n$
FC-1	4	2.7074	0.7394	4.64	3500	1.41
FC-2	4	2.5965	0.8006	26.8	4300	1.60
FC-3	2	2.5300	0.7400	3.7	4500	1.51
FC-4	2	5.0160	0.7642	5.1	3400	1.44
FC-5	2.5	15.0021	3.0560	13.6	3000	1.45

Grafting by ATRP method: The Schlenck tubes dried with hot air which is containing the reaction mixture of monomer (S), poly(ε-CL-b-ECH-b-ε-CL) block copolymer, CuCl, and bipyridine were degassed by vacuum and nitrogen (to create an inert atmosphere), and sealed under vacuum. Then all the test tubes were placed in a silicone oil bath set at a temperature of 110 ° C. When the polymerization completed, Schlenck tubes were cooled. The tubes' contents were diluted with ethyl acetate.

These Solvents were filtered and precipitated with methanol to separate the polymer products. The block-graft copolymers were dried at 40^{0}C in a vacuum oven for three days. The conditions and data from which the polymerisation is obtained can be seen in Tables 2 and 3.

Table 2. ATRP of styrene with poly(ε-CL-b-ECH-b-ε-CL) block copolymer (FC-5 in Table 1) at 110°C . Time: 14 hours

Code	S/poly(ε-CL-b-ECH-b-ε-CL) (mol/mol)	poly(ε-CL-b-ECH-b-ε-CL) (g)	S (g)	CuCl (g)	bPy (g)	Yield of polymer (%)	$\overline{M}_{n\ GPC}$	$\overline{M}_w/\overline{M}_n$
FAB-2	200/1	0.1442	1.0212	0.0048	0.0150	3,8	3100	1.44
FAB-3	50/1	0.5772	1.0179	0.0190	0.0600	25,5	3800	1.70
FAB-4	75/1	0.3848	1.0043	0.0127	0.0400	15,75	3200	1.58
FAB-5	100/1	0.2886	1.0424	0.0095	0.0300	12,5	3200	1.59

Table 3. ATRP of styrene with poly(ε-CL-b-ECH-b-ε-CL) block copolymer (FC-1 in Table 1) at 110°C. Poly(ε-CL-b-ECH-b-ε-CL) = 2.5x10^{-2} g (7.0x10^{-6} mol), CuCl=7.0x10^{-4} g (7.0x10^{-6} mol), bpy=2.2x10^{-3} g (1.4x10^{-5} mol), time: 22 hours

Code	S (g)	Yield of polymer (%)	$\overline{M}_{n\ GPC}$	$\overline{M}_w/\overline{M}_n$
FT-1	0.5049	3,2	30000	3.60
FT-2	0.7651	37,5	51000	2.13
FT-4	1.2504	33,7	59000	1.88
FT-6	2.0146	42,11	62000	1.73

Characterization of the polymers: A Waters brand system consisting of a Waters 2414 refractive index detector, a Waters model 1515 isocratic pump and HR3, HR4E and HR4 strafrag columns was used as the GPC instrument. The 1H-NMR spectra of the polymers were obtained on a Varian/Mercury-200 (200 MHz) NMR spectrometer in CDCl$_3$ solution. Perkin Elmer Diamond differential calorimetry was used for differential scanning calorimetry (DSC) analyzes. (Under a nitrogen atmosphere, in the temperature range 20 - 250 ^{o}C)

RESULTS AND DISCUSSIONS

Synthesis of Poly(epichlorhydrin) (PECH): According to scheme 1, PECH with chain end hydroxyl group was synthesized by cationic polymerization of ECH. HBF4 was used as the catalyst in the reaction and the results were confirmed by 1H-NMR and GPC measurements. According to the 1 H-NMR spectrum of PECH in FIG. 1, It indicates characteristic signals of 4.07-3.60 ppm (broad) for the protons -OCH$_2$, CH$_2$ -CH$_2$ Cl and -CH$_2$ Cl of PECH.

Cationic polymerization of ECH was carried out by dropwise addition of ECH to the HBF4 solution. The actively extending PECH chain was stopped with water and OH terminal PECH was obtained.

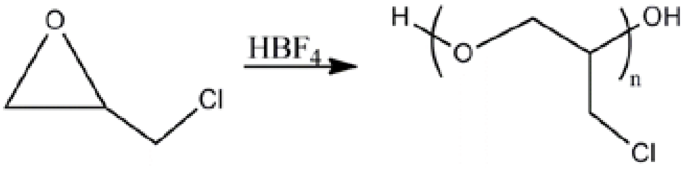
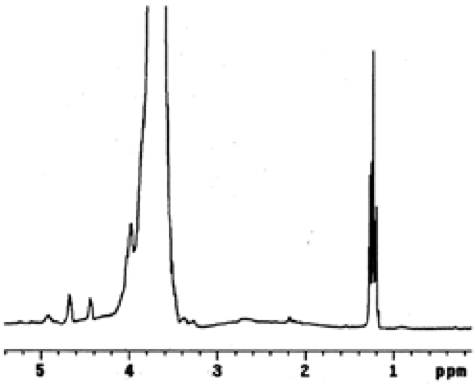
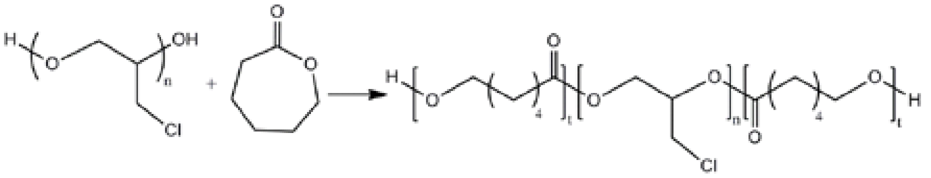


Figure 1. ^{1}H-NMR spectrum of PECH



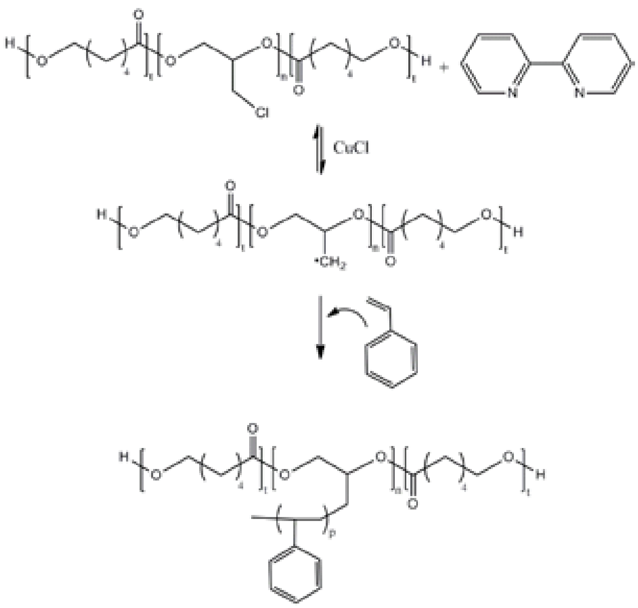
Scheme 1. Cationic polymerization of epichlorohydrin (ECH).

Synthesis of PCL-PECH-PCL block copolymers: PCL- PECH- PCL block copolymers were synthesized by the ROP of ε-CL with PECH possessing two hydroxyl functional groups in different conditions according to Table 1. The synthesis of block copolymers was performed in the presence of $Sn(oct)_2$ ($110^{o}C$). The polydispersities of the PCL-PECH-PCL block copolymers were determined between 1.41 and 1.60. The reaction pathway is represented in Scheme 2.



Scheme 2. ROP of ε-caprolactone with PECH.

Synthesis of [PCL-b-PECH-b-CL]-g-PS block-graft copolymers: The approach for the synthesis of block-graft copolymers is shown in scheme 3. Tables 2 and 3 include the results from several polymerizations using poly(ε-CL-b-ECH-b-ε-CL) block copolymer as macroinitiator. The physical state of yielded block-graft copolymer was white solid.



Scheme 3. ATRP of styrene with poly(ε-CL-b-ECH-b-ε-CL)/CuCl/bpy initiating system.

Characterization of the Polymers: Yielded polymers can be undergone polymer films. The characterization of polymeric macromolecules with mostly transparent properties can be summarized as follows. When compared to Macro initiator, the determined increases in molecular weights will prove the formation of the block-graft copolymer of the products. The 1 H-NMR, and GPC measurement techniques were used for the characterization of block and block-graft copolymers. In Fig. 1, the characteristic signals of PECH at 4.00-3.40 ppm in 1 H-NMR analysis show PECH protons (-CH 2 -, -CHO-, -CH 2 Cl). The -OH proton signals in the spectrum can be seen at 1.2 ppm. The structure of the PCL-b-PECH-b-PCL block copolymer was characterized by ^{1}H-NMR (see Figure 2).

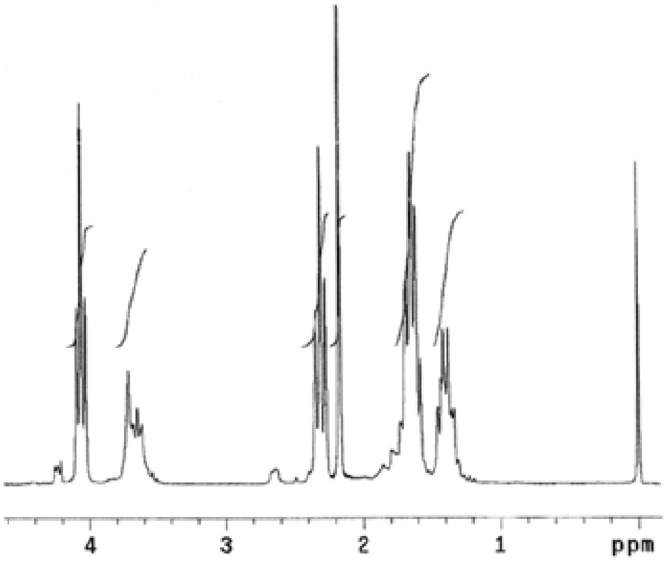


Figure 2. ^{1}H-NMR spectrum of PCL-b-PECH-b-PCL block copolymer

As shown in Figure 2, signals are observed at 4.01-4.08 ppm(triplet), originating from methylene protons(-OCH$_2$-) of PCL chain, and a signal observed 3.63-3,70 ppm is assigned to the -OCH$_2$- protons of PECH chain. Figure 3 shows ^{1}H-NMR spectrum of [(PCL-b-PECH-b-PCL)]-g-PS block-graft copolymer, which exhibits signals at 6.59-7.26 ppm (aromatic –CH for PS), 4.03-4.09 ppm (-OCH$_2$- for PECH) and 2.27-2.34 ppm (O=CCH$_2$- for PCL).

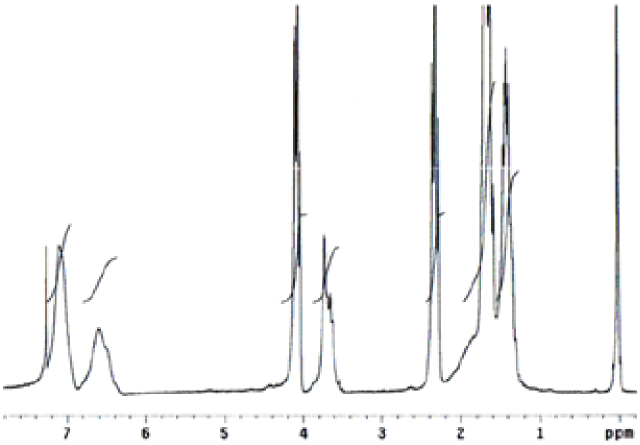


Figure 3. ^{1}H-NMR spectrum of [(PCL-b-PECH-b-PCL)]-g-PS block-graft copolymer

The molecular weight values (Mn) of the block and block-graft copolymer are determined by GPC as shown in Figure 4.

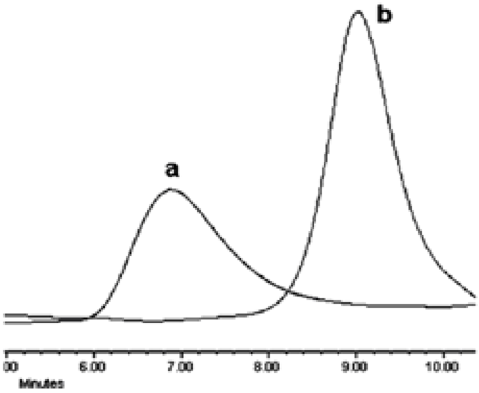


Figure 4. GPC curves of (a) [ε-CL-b-ECH-b-ε-CL]-g-PS (Table 3- FT-4) M_n: 59346 g/mol (b) ε-CL-b-ECH-b-ε-CL M_n: 3529 g/mol (Table 1 FC-1).

Chromatograms show the increasing average molecular weight due to block graft copolymerization and narrow molecular weight distribution. According to the GPC results the block-graft copolymers have the polydispersity values in a range of 1,44-170. The low polydispersity value of the block-graft copolymers is a result and evidence of ATRP. Narrow/low polydispersity values indicate that the polymer chains have similar molecular weights.

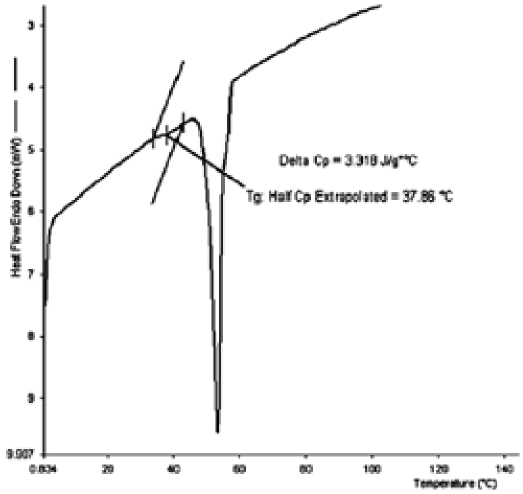


Figure 5. DSC curve of the PCL-b-PECH-b-PCL block copolymer.

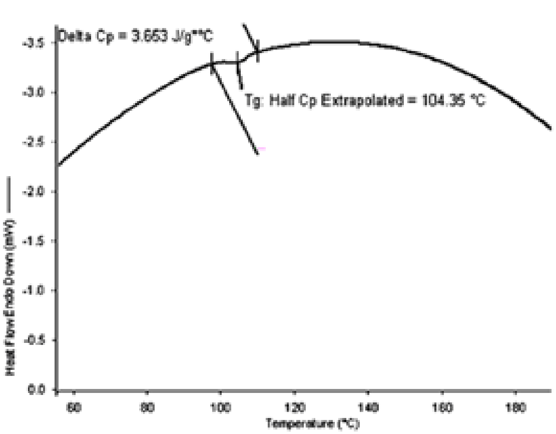


Figure 6. DSC curve of the [(PCL-b-PECH-b-PCL)]-g-PS

The glass transition temperature (T_g) of PS is 100 °C. PECH was an amorphous polymer, exhibiting a T_g at -23 °C. The T_g's of the PCL-b-PECH-b-PCL and [(PCL-b-PECH-b-PCL)]-g-PS are shown Figure 5 and Figure 6. Due to narrow polydispersities (1,44-1,70) of yielded block-graft copolymer ([(PCL-b-PECH-b-PCL)]-g-PS) is showing a higher Tg (104,35 °C) than styrene's homopolymer (100 °C). In addition, the obtained results indicate that Tg values of block and block-graft copolymers were different than those of their homopolymers. This is an evidence for the formation of block and block-graft copolymers.

CONCLUSION

The synthesis of block-graft copolymers has drawn an increasing attention of the researchers in recent years. This is because of the fact that block-graft copolymers are having special chemical structures yield unusual physical properties.

The [(PCL-b-PECH-b-PCL)]-g-PS block-graft copolymers were obtained by a subsequent three methods without any modification of the initiating site, using AMP, CRP and ATRP methods. In conclusion, poly(ε-CL-b-ECH-b-ε-CL) block copolymer were used as the macroinitiator for ATRP of styrene, resulting poly(ε-CL-b-ECH-g-PS-b-ε-CL) block-graft copolymers, succesfully.

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