Modification of Functional Polyesters Bearing Norbornene Moieties via Olefin Metathesis Reactions

Olefin Metatez Tepkimeleri ile Norbornen İçeren Fonksiyonel Poliesterlerin Modifikasyonu

Research Article

Bengi Özgün Öztürk*
Department of Chemistry, Faculty of Science, Hacettepe University, Ankara, Turkey.

ABSTRACT

In this study, unsaturated functional polyester derivatives were synthesized via polycondensation reactions of 5-norbornene-2,3-dicarboxylic anhydride and 1,6-hexanediol. Functional unsaturated polyesters were modified using methyl acrylate as ring opening/cross-metathesis reaction partner. The solubility and hydrophobic/hydrophilic character of polyester was tuned by integrating allyl end capped poly(ethyleneglycol) by ring opening/cross-metathesis reactions. Norbornene moiety of unsaturated polyesters allowed us to use ring opening metathesis polymerization reactions to form side-chain poly(norbornene) on main polyester chain using Grubbs 1st, 3rd and Hoveyda-Grubbs 2nd generation catalysts as initiators, resulting in gel-like materials.

Key Words
Ring opening/cross-metathesis, polyesters, ruthenium, polycondensation.

ÖZ

Bu çalışmada doymamış fonksiyonel poliester türevleri 5-norbornen-2,3-dikarboksilik anhidrit ve 1,6-hekzandiol bileşiklerinin polikondenzasyon tepkimeleri ile elde edilmiştir. Fonksiyonel doymamış poliesterler metil akrilat kullanılarak halka açılma/çapraz metatez tepkimeleri ile modifiye edilmiştir. Poliesterlerin çözünürlük ve hidrofobik/hidrofilik karakterleri halka açılma/çapraz metatez tepkimeleri ile alil son grubuna sahip poli(etilenglikol) bileşikleri entegre edilerek değiştirilmiştir. Doymamış poliesterlerdeki norbornen grubu sayesinde jel benzeri malzemeler, Grubbs birinci, üçüncü ve Hoveyda-Grubbs ikinci nesil katalizörleri varlığında halka açılım metatez polimerizasyon tepkimeleri ile ana poliester zinciri üzerinde yan poli(norbornen) zincirlerinin oluşumu ile elde edilmiştir.

Anahtar Kelimeler
Halka açılım/çapraz metatez, poliester, rutenyum, polikondenzasyon.

INTRODUCTION

The functionalization of synthetic polymers is in great importance owing to their application fields such as smart materials design, drug-delivery, biomaterials and gene-therapy [1-4]. In order to adapt polyester derivatives to above mentioned applications polymers should have amorphous, water-soluble and must have reactive groups to functionalize polymer chain [5]. The traditional polymers such as poly(L-lactic acid) (PLLA) poly(glyclolic acid) (PGA), poly(caprolactone) (PCL) are synthesized by ring-opening polymerization (ROP), mostly yielding hydrophobic and semi-crystalline polymers [6]. For the past decade, several studies are focused on the synthesis of amorphous aliphatic polyesters that can be used in several fields [7]. The integration of functional polar group on polymer chain is used as an efficient strategy. Amsden and research group have reported acrylate terminated star shaped polymers bearing amorphous poly(DL-lactic acid) (PDLLA) [8]. The cross-linking ability of the material was investigated by varying the length of the arms of the stars and photo-curing conditions. Sebacic acid and glycerol was used by Langer et. al for the synthesis of a though biodegradable elastomer, exhibiting total amorphous property at 37°C [9]. In 2007 Sheares et. al. have used linear diols and dicarboxylic monomers to obtain unsaturated aliphatic polyesters via step growth polycondensation [10]. In addition to anhydride-diol combination, epoxy based materials were also polymerized with anhydride based monomers [11]. Unsaturated polyesters are in great importance in polymer chemistry since they can be used to synthesize functional materials by modification through double bonds [12]. Cross-metathesis is a valuable partner for modification of unsaturated polymers [13-14] β-heptenolactone (βHL) based polyesters were modified via olefin cross-metathesis reactions altering the thermal, chemical and physical properties of polymers [15]. In addition to repeating unit modification reactions, cross-metathesis reactions are also used for end-capping of polymers [16]. Recently, greener approaches have been developed for polyester synthesis utilizing furfural [17] and epoxides [18].

Here in, we report an efficient method for post-modification of unsaturated polyester derivatives via ring opening/cross-metathesis and ring opening metathesis polymerization. The effect of cross-metathesis modification on T_g and solubility of the polymer was investigated in details. Thermoplastics with relatively higher thermal stabilities were obtained by ROMP of norbornene moiety of unsaturated polyesters in the presence of Grubbs 1st, 3rd and Hoveyda-Grubbs 2nd generation catalysts.

MATERIALS and METHODS

Chemicals and Instruments

Otherwise noted all chemicals were purchased from Sigma-Aldrich and used as received. Umicore@M1 was purchased from Strem Chemical Inc. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 25°C with a Bruker GmbH 400 MHz high-performance digital FT-NMR spectrometer using $CDCl_3$ as the solvent. Molecular weights were determined with a GPC System LC-20A from Shimadzu equipped with SIL-20A autosampler, RID-10A, and a refractive index detector. The analysis was performed on the following column system operating on THF (flow rate 1 mL min^{-1}) at 40°C: main-column PSS SDV analytical (5 μm, 300 mm × 8.0 mm, 10 000 Å) and a PSS SDV analytical precolumn (5 μm, 50 mm × 8.0 mm). The calibration was created using narrow linear poly(methyl methacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981 000 Da.

Synthesis of P1

A Schlenk reactor was charged with 5-norborn-ene-2,3-dicarboxylic anhydride (1.0 g, 6.10 mmol) and 1,6-hexanediol (7.30 mmol, 0.865 g). The reaction mixture was taken to a pre-heated oil bath (120°C) and stirred for 10 min prior to addition of catalyst; $Sn(Oct)_2$ (0.061 mmol). After addition of catalyst to the reactor, Schlenk reactor was connected to a vacuum pump (vacuum value; 30-40 torr) and reaction mixture was stirred for 12 h under these conditions. After 12 h, reaction mixture was cooled down and poured into cold-methanol and stirred for additional 30 min. P1 was isolated by simple filtration, followed by washing with cold methanol/acetone mixture. P1 was characterized by ^1H, ^{13}C NMR and GPC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.17 (m, 2H), 4.31 – 3.79 (m, 24H), 3.43 (d, J = 18.2 Hz, 2H), 3.33 – 2.95 (m, 2H), 1.55-1.29 (m, 10H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 175.23 – 170.19 (m), 137.78 (d, J= 30.8 Hz), 134.92 (d, J= 16.4 Hz), 66.15 – 61.50 (m), 49.86 (d, J= 140.0 Hz), 51.81 – 43.47 (m), 32.13 – 27.77 (m), 26.49 – 22.44 (m).

Cross-Metathesis Reactions of P1

A Schlenk reactor was charged with P1 (0.10 g, M$_n$: 4000 Da) in toluene (5 ml). The reactor was taken to a pre-heated oil bath at 85°C and stirred for 10 min prior to addition of Hoveyda-Grubbs 2nd generation catalyst (commercial code C711, 0.01 g, 0.014 mmol). After addition of the catalyst, reaction mixture was stirred for 12 h at 85°C. The reaction was terminated by addition of excess ethyl vinyl ether (2 ml). Resulting polymer (P2) was precipitated in cold methanol and filtrated. Same reactions were also applied for PEG modification of P1, resulting in P3.

Ring Opening Metathesis Polymerization of P1

A Schlenk reactor was charged with P1 (0.10 g, M$_n$: 4000 Da) in CH$_2$Cl$_2$ (1 ml). Grubbs 3rd generation catalyst (0.01 g, 0.011 mmol) dissolved in CH$_2$Cl$_2$ (1 ml) was added to the reaction mixture. Gelation occurred within 1-2 hours. Reaction mixture was kept under same conditions for 24 h to make sure for the termination of gelation reaction.

RESULTS and DISCUSSION

Optimum reaction conditions were investigated for the polymerization of 5-norbornene-2,3-dicarboxylate, 5-norbornene-2,3-dicarboxylate, 5-norbornene-2,3-dicarboxylic acid with 1,6-hexanediol in the presence of tin(II) ethylhexanoate, titanium (IV) isopropoxide and 1,5,7-triazabicyclodecene (TBD) (Scheme 1).
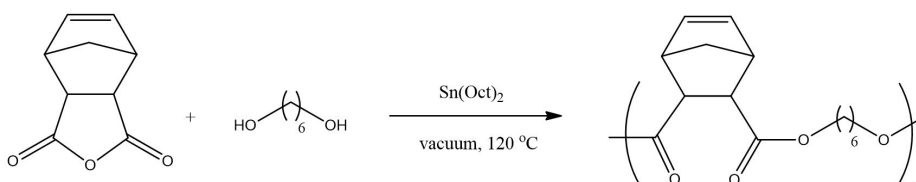
The optimal polymerization reaction found to proceed at 120°C with a catalytic loading of 1% Sn(Oct)$_2$ at reduced pressure (40 Torr) for 24h. The results were listed in Table 1. Polyesters with varying M$_n$ values between 2000-11000 Da. All polymers are at viscously oil form at room temperature. ^{1}H NMR spectrum of P1 can be seen in Figure 1. Olefinic proton signals of norbornene ring appeared at 6.17 ppm. –CH$_2$COO– group of aliphatic fragment was observed at 3.86-4.00 ppm as multiplets. Other norbornene protons were observed between 3.40-3.09 and 1.29-1.54 ppm. Aliphatic fragment of polymer showed signals at 1.29-1.54 ppm. ^{13}C NMR spectrum of P1 showed a singlet peak at 172.50 ppm indicating the presence of –C=O group. Olefinic carbon signals appeared at 134.90 ppm (Figure 2). A second olefinic peak appeared at 137.78 ppm, which belongs to the norbornene unit of polymer chain end-group. –OCH$_2$ signal was appeared at 64.29 ppm, Differential Scanning Calorimetry (DSC) analysis of P1 showed a glass-transition temperature (T$_g$) at -19.70°C. The olefinic moiety of polyester chains allows one to modify polymer via olefin metathesis reactions. The integration of several functional groups to polymer chains extend the applications of these polyester based materials. P1 was modified using cross-metathesis reactions. Olefinic norbornene moiety of P1 was reacted with methylacrylate and allyl poly(ethyleneglycol); allyl-PEG. Grubbs 1st generation (G1), Grubbs 2nd generation (G2), Grubbs 3rd generation (G3) and Hoveyda-Grubbs 2nd generation (HG2) catalysts were used in olefin metathesis reactions of P1. In order to optimize the reaction conditions; several reaction parameters such as; temperature, catalytic loading %, olefin/polyester ratio and solvent effect were investigated in details.

Scheme 1. Polycondensation reactions.

Table 1. Polycondensation reactions (P1).

| Entry	Catalyst	Catalyst (%)	M_n (GPC)(Da)[a]	PDI[a]	Yield (%)
1	TBD	0.5	11200	2.4	80
2	TBD	1	6000	2.1	90
3	TBD	2	4000	2.0	95
4	Sn(Oct)$_2$	0.5	8700	2.2	85
5	Sn(O$_c$t)2	1	5500	2.1	90
6	Sn(Oct)$_2$	2	4100	1.9	94
7	Ti(O-i-Pr)$_4$	0.5	8200	2.2	75
8	Ti(O-i-Pr)$_4$	1	6100	2.1	85
9	Ti(O-i-Pr)$_4$	2	3700	1.7	88

a: Determined by GPC analysis in THF (1.0 ml/min) against lineer poly(methylmethylacrylate) standarts.
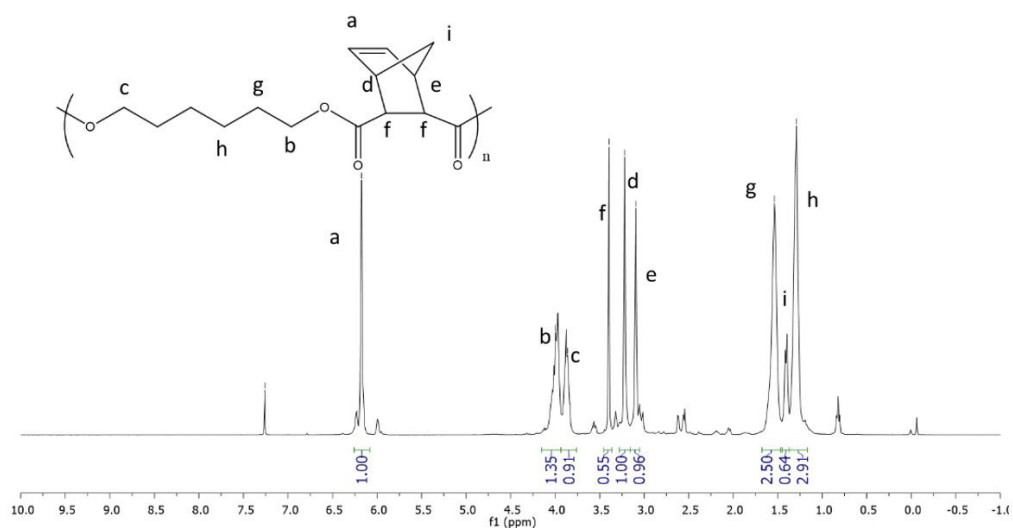
Figure 1. ^{1}H NMR spectrum of P1.
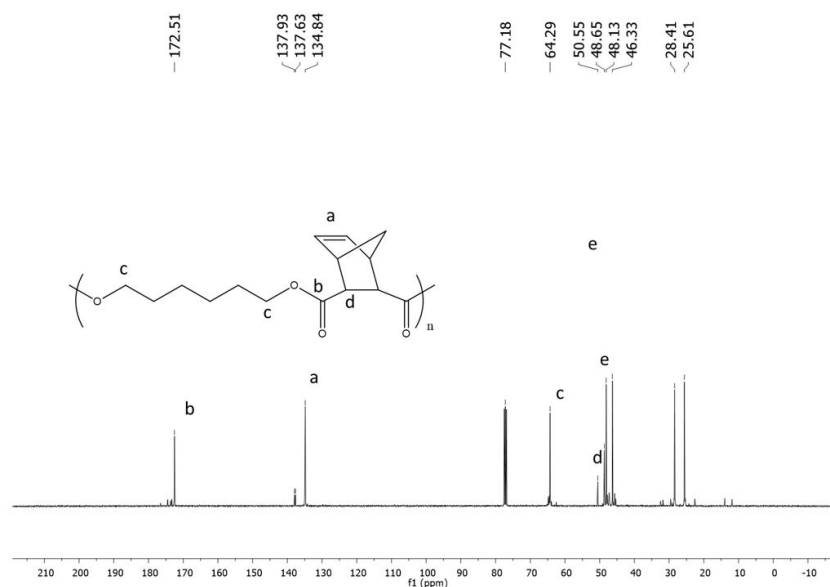
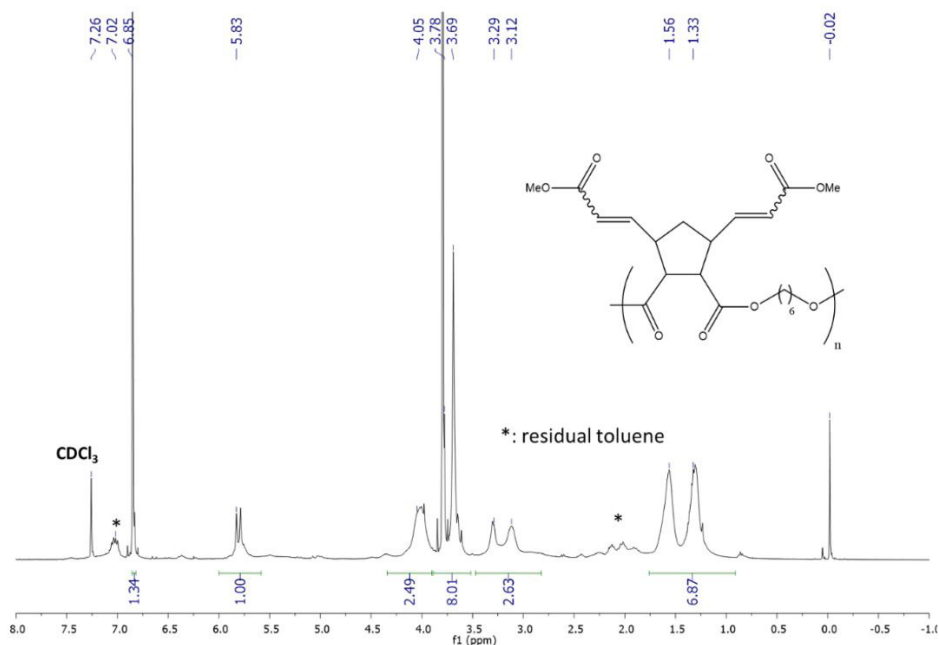**Figure 2.** ^{13}C NMR spectrum of P2.

The olefinic moiety of polyester chains allows one to modify polymer via olefin metathesis reactions. The integration of several functional groups to polymer chains extend the applications of these polyester based materials. P1 was modified using cross-metathesis reactions. Olefinic norbornene moiety of P1 was reacted with methylacrylate and allyl poly(ethyleneglycol); allyl-PEG. Grubbs 1st generation (G1), Grubbs 2nd generation (G2), Grubbs 3rd generation (G3) and Hoveyda-Grubbs 2nd generation (HG2) catalysts were used in olefin metathesis reactions of P1. A set of terminal olefins, methyl acrylate, methyl end capped poly(ethylene glycol) Mn: 500 Da), allyl bromide and acrylic acid was chosen for ring-opening cross metathesis (ROM-CM) reactions. Well-known ruthenium metathesis initiators; Grubbs 1st (G1), 2nd (G2) and 3rd (G3) and Hoveyda-Grubbs 2nd generation (HG2) complexes were employed in order

to find the best performing catalyst. First model reaction was carried out using methyl acrylate as cross-metathesis partner and P1 in toluene at 80°C in the presence of 1 % G1, G2, G3 or HG2 (Scheme 2).

The catalysts were compared in means of thermal stability, robustness and activity. Among the tested catalysts HG2 was chosen as best catalyst in means of conversion, selectivity and stability. After 24h of intense stirring at 80°C, reaction was terminated by addition of excess ethyl vinyl ether to reaction media and stirred for an additional 30 min. Polymer was precipitated in cold-methanol. Isolated polymer was labelled as P2. The conversion was determined by ¹H NMR by evaluating olefinic proton signals of norbornene and the side-groups of resulting cyclopentane ring. As it can be concluded from ¹H NMR spectrum, ROM-CM reaction of P1 with methyl acrylate proceeded with di-substitution of cyclopentane ring (Figure 3) with full conversion.
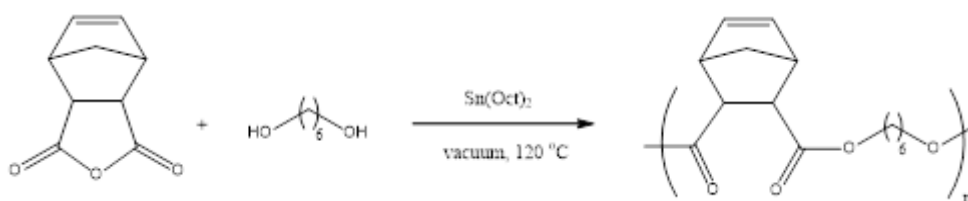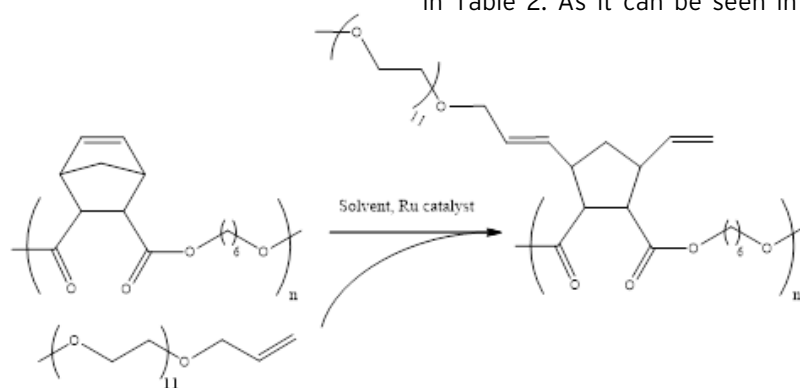

Scheme 2. Synthesis of P2.

Figure 3. ¹H NMR spectrum of P2.

Olefinic proton signals were observed at 6.85 (2H, d, J=) and 5.83 (2H, d, J=) ppm, indicating predominant trans-configuration. -OCH$_2$- group appeared at 4.05 ppm (4H, as multiplet) and 3.78 ppm. -OCH$_3$ group was observed at 3.69 ppm. Although promising results were obtained with methyl acrylate, modification of P1 with other olefins; allyl bromide and acrylic acid were failed due to catalyst decomposition. All catalysts; G1, G2, G3 and HG2 were poisoned in the presence of these olefinic materials. In the search for water soluble polyester derivatives, we used methyl end capped allyl-PEG (500 Da) for modification of P1 via ROM-CM (Scheme 3). The reaction was carried out at predetermined optimum reaction conditions that for P2. Once the reaction is completed, P3 was isolated by pouring the reaction mixture to diethyl ether and stored at -24°C overnight for precipitation.

^{1}H NMR results showed that norbornene moiety underwent ROM-CM reactions to form vinyl substituted cyclopentane ring (Figure 4). Vinylic double bond proton peaks appeared at 5.01-5.12 ppm as multiplets, hydrogen atoms bonded to PEG substituted vinyl group appeared at 6.05-5.71 ppm. Hydrogens, the vinyl neighbouring ones, were appeared at 3.85 ppm. The repeating group of PEG (-OCH$_2$CH$_2$-) were appeared at 3.47 ppm as a very intense peak. -OCH$_2$ group of polyester chain was observed at 3.20 ppm.

The solubility of P1, P2 and P3 was compared in Table 2. As it can be seen in Table 2, P1 and

Scheme 3. Synthesis of P3.
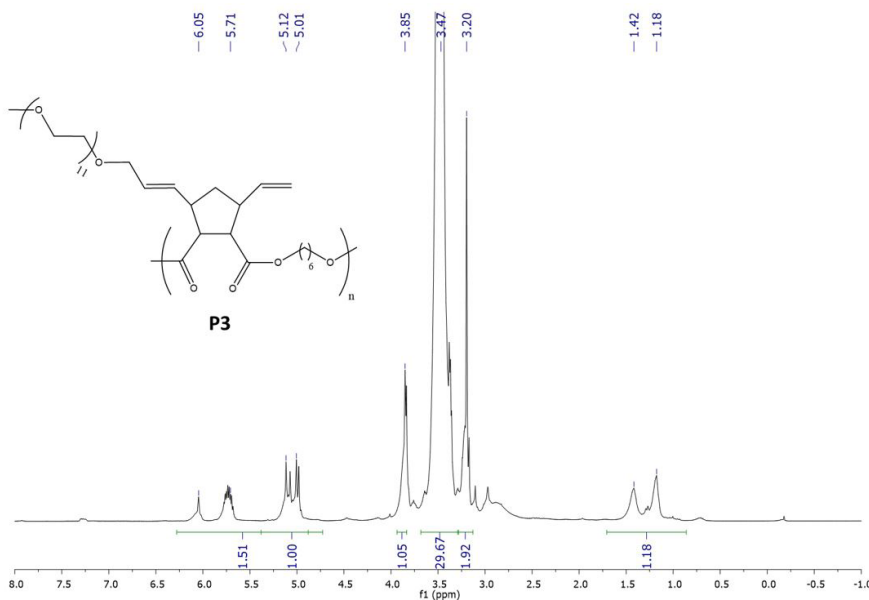
Figure 4. ^{1}H NMR of P3.

P2 is readily soluble in common organic solvents such as toluene, tetrahydrofuran, dichloromethane, chloroform and slightly soluble in acetone and insoluble in hexane and water. P3 is soluble in water and common organic solvent; dichloromethane, chloroform, toluene, THF and insoluble in n-hexane.

Following the modification P1 with allyl PEG group (P3), the glass transition temperature (T_g) was reduced from -13.20°C to -19.70°C due to the contribution of PEG group on overall conformational flexibility of polymer structure.

Table 2. Solubility of polyesters (P1, P2 and P3).

Entry[a]	CH_3OH	$CHCl_3$	CH_2Cl_2	Acetone	Toluene	H_2O	THF	Hexane
P1	-	+	+	=	+	-	+	-
P2	-	+	+	=	+	-	+	-
P3	+	+	+	=	+	+	+	-

a: -: non-soluble, =: partially soluble, +: soluble.

Table 3. Thermal stability of P1 after cross-linking.
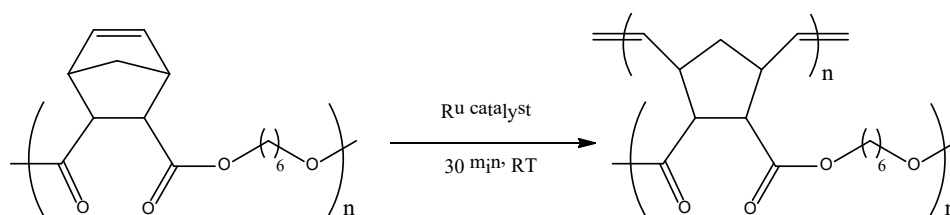
Entry	Catalyst	Weight loss (°C)[a]		
		5 (%)	10 (%)	40 (%)
1		230	275	400
2		300	350	430
3		240	290	410
4	-	195	240	360

a: Determined by TGA.

On the next trial, ring-opening metathesis reactions of P1 was carried out using Grubbs 1st,3rd, Hoveyda-Grubbss 2nd generation catalysts to investigate the gelation behaviour of P1. It is well known in literature that highly strained norbornene ring can undergo ring opening metathesis reactions in the presence of Grubbs type ruthenium catalysts, forming oligomeric/polymeric vinly substituted cyclopentane rings. In the case of P1, which is a polyester derivative with repeating norbornene rings, norbornene group can undergo ring opening-cross metathesis via inter-molecular or intra molecular pathways, resulting in a cross-linked polymeric material. The effect of cross-link on thermal stability of the polymers was investigated using TGA analysis. As it can be seen in Table 3, the 5, 10 and 40% weight loss values shifted to higher temperature values, indicating the effect of cross-linking on overall structure of P1.

CONCLUSION

Unsaturated polyesters derived from polycondensation of 1,6-hexanediol and 5-norbornene-2,3-dicarboxylic anhydride were successfully modified via ring opening/cross metathesis reactions. It has shown that polymer properties (T_g, solubility, polarity) can be tuned by integrating functional groups via cross metathesis. In addition, thermoplastic like materials were synthesized from unsaturated polyesters using Grubbs type ruthenium metathesis catalysts. The effect of cross-link, which was exerted by ring-opening metathesis polymerization of norbornene moiety was demonstrated by TGA analysis.

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