

Chain Extension Reactions of Unsaturated Polyesters with Bis(2-Oxazoline)s

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ABSTRACT: Two different bisoxazolines, 2,2'-(1,3-phenylene) bis(2-oxazoline) (1,3-PBO) and 2,2'-bis(2-oxazoline) (BO) were investigated as chain extenders for short chain unsaturated polyesters (UPEs). These extenders reacted readily with carboxyl ends of unsaturated polyesters, leading to rapid molecular weight increase through coupling of oligomeric chains. Commercially available unsaturated polyesters commonly have molecular weights around 1500, usually reached after a 20-h polyesterification reaction. When bisoxazolines were reacted with short UPE chains obtained at the 6th hour of a commercial polyesterification

reaction, the molecular weight of UPE reached 1500 within 5–30 min, which provides economies and prevents the glycol loss and yellowing which are associated with extended reaction times. Styrene solubility, gel time, and thermal and mechanical properties of the chain extended polyesters remained comparable to the commercial UPE, with 8–10 min of gel time and a storage modulus about 3000 MPa. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3229–3235, 2012

Key words: unsaturated polyesters; bisoxazolines; chain extender; molecular weight increase

INTRODUCTION

Unsaturated polyesters (UPE) are products of polyesterification reactions of saturated and unsaturated diacids (or anhydrides) with diols. These low molecular weight polymers (MW 1500) are dissolved in vinyl monomers such as styrene and sold as liquid molding resins ready for free radically initiated cross-linking. UPEs are commonly used in pipes, sports equipment, automotive, construction, and marine industries as glass or carbon fiber reinforced composite materials and have excellent mechanical properties.¹

The polyesterification reaction is rather demanding, and requires temperatures as high as 220 °C for about 20 h to reach the desired molecular weight. As compelled by the equilibrium reaction, water has to be removed under application of vacuum in order to increase the molecular weight. Polymerization catalysts such as tin, titanium, and antimony alkoxides increase the reaction rate, but create problems such as discoloration and necessity of removal.² In industrial applications all these difficulties contribute to the cost of manufacture and constitute an important drawback for the polyesterification reaction.

To reach the desired molecular weight in a much shorter time than 20 h, chain extenders can be used. These monomers should have a low molecular weight and at least two functionalities capable of reacting with polyester end groups, preferably without producing by-products. Low molecular weight is also desirable, so that the required chain extender amount is as small as possible. In this fashion, longer polymers with the desired molecular weight can be obtained in a relatively short time. Shortening of the reaction time provides economies in energy and avoids the usual problem of yellowing and monomer loss observed towards the end of large scale polyester synthesis. Additionally if the chain extension proceeds without a by-product, the actual yield of the polymer increases upon using a chain extender. Chain extenders can be added to the reactor at an arbitrary time, where polymer chains have an optimum length, to enable a rapid molecular weight increase upon addition of a minimum amount of chain extender. Even though chain extenders are usually used in small amounts, they introduce new linkages to the polymer chain,³ which could alter solubility, gel time, and finally the mechanical and thermal properties of the final (cross-linked) product.

Three epoxy compounds, namely, diglycidyl ether of bisphenol A; epoxidized soybean oil and 1,2;7,8-diepoxyoctane were investigated as chain extenders for UPEs earlier in our laboratories.⁴ These extenders readily reacted with the carboxyl end groups of the polyester chains and gave promising results for faster manufacture of UPEs. In another study by our

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group two blocked diisocyanates, namely diphenylmethane-bis-4,4'-ethyleneurea and diphenylmethane-bis-4,4'-carbamoil- ϵ -caprolactam and isocyanated soybean oil were employed as chain extenders for UPEs and they also favored rapid molecular weight increase in relatively short times.⁵ Many difunctional molecules such as diepoxides, dianhydrides, and diisocyanates have been reported to increase the molecular weight of polyethyleneterephthalate (PET). These chain extenders are especially useful when fiber grade PET is desired and when recycled PET is used in the formulation. These molecules rapidly react with the end groups of degraded PET chains to regain the desired molecular weights within minutes.^{6,7}

Cyclic bis(imino ether)s, also called bis(2-oxazoline)s, are difunctional monomers, which are capable of reacting with several kinds of reactive groups. In a recent study, bis(2-oxazoline)s were shown to react with diacids via addition mechanism to give linear poly(ester-amide)s.⁸ One important advantage of this reaction is that no by-products are produced and the reaction between carboxylic ends and bisoxazolines takes place readily at temperatures far below 220°C, the required temperature for polycondensation. Bis(2-oxazoline)s were subject to various studies related to polyethylene terephthalate (PET) to favor melt viscosity increase especially in fiber manufacture with recycled PET.

The reaction of 2,2'-(1,3-phenylene)-bis(2-oxazoline) (1,3-PBO) and 2,2'-bis(2-oxazoline) (BO) with carboxylic end groups of UPE is shown in Figure 1. It is also contemplated that the aromatic amide introduced during chain extension may provide hydrogen bonding sites and increase chain rigidity and lead to an increase in the storage modulus and heat deflection temperature of the final cross linked polyester.

The aim of this work is to report the effect of bis(2-oxazoline)s as chain extenders on unsaturated polyesters and to examine solubilities and mechanical and thermal properties of the chain extended polyesters in order to verify that these properties remained unaltered when compared to a commercial reference product.

EXPERIMENTAL

Materials

The starting materials for chain extension reactions were short chain unsaturated polyesters with an acid number of 80 and molecular weight of about 1000. These short chain polyesters were taken from a 36 ton reactor at the 6th hour of a 20 h industrial synthesis. They were supplied by Cam Elyaf A.S., (Istanbul, Turkey) a major producer of polyesters in Turkey.

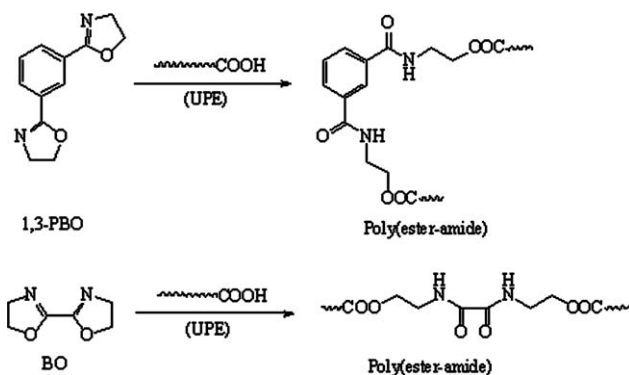


Figure 1 Chain extension reactions with bis(2-oxazoline)s.

2,2'-(1,3-phenylene)-bis(2-oxazoline) was bought from Degussa AG (Dusseldorf, Germany) and 2,2'-bis(2-oxazoline) was bought from TCI Europe (Zwijndrecht, Belgium).

Methyl ethyl ketone peroxide (MEKP) and Cobalt naphthenate (6% solution in dibutyl phthalate) were supplied by Cam Elyaf A.S., (Istanbul, Turkey).

GPC samples were prepared by dissolving the unsaturated polyester samples in tetrahydrofuran, bought from J. T. Baker (Deventer, Holland).

Instruments

The molecular weight increase was monitored by gel permeation chromatography, a Viscotec VE-2001 (GPC max) Analysis system (Viscotek, Houston, TX) with a PL Gel 5 micrometre MIXED-C Column that was calibrated against polystyrene standards. THF was used as solvent at room temperature with a flow rate of 1 mL/min.

¹H-NMR spectroscopy was run using Varian Mercury-Vx 400 MHz NMR Instrument (Varian Associates, Palo Alto, CA). IR characterization of compounds was performed by Thermo Nicolet, FTIR 380 spectrometer, using the diamond ATR accessory. The DMA tests were done between 25 and 180°C on 40 × 12 × 2 mm³ samples using DMA Q800, TA Instruments (New Castle, Delaware, USA) in single cantilever mode at a frequency of 1 Hz and at 25°C with a heating rate of 3°C/min. The measurements range was between room temperature and 155°C. Thermal gravimetric analyses were carried out using "Thermal Analyses" Q-50 Instrument, TA Instruments (New Castle, Delaware, USA) with a heating rate of 10°/min starting from room temperature to 600°C where nitrogen gas was purged at a rate of 60 mL/min.

Chain extension reactions

In a typical reaction, oligomeric UPE with an acid number of 80 and molecular weight of 900–1000 was

TABLE I
 M_n Values With Different Extender Amounts

Reaction time (min)	M_n				
	Control (no extender)	15% 1,3-PBO (pdi ^b) stoichiometric amount	3% ^a 1,3-PBO (pdi ^b)	10% BO (pdi ^b) stoichiometric amount	4% ^a BO (pdi ^b)
0	1030	1030 (1,5)	1030 (1,5)	1030 (1,5)	1030 (1,5)
5	1030	1700 (1,8)	1400 (1,8)	1420 (1,9)	1410 (1,6)
30	<1150	1700 (1,8)	1500 (2,0)	1400 (1,7)	1470 (1,7)
60	<1150	–	1600 (2,3)	1600 (1,7)	1520 (1,8)

^a Optimum amounts.

^b Pdi, poly dispersity index.

mixed with bisoxazoline at 160°C under nitrogen and stirred for 30–60 min, without catalyst. Acid number determination was done according to ASTM D 974-64.⁹ The unsaturated polyester sample was dissolved in 1 : 1 acetone:toluene mixture and titrated against 0.5N KOH, in the presence of two to three drops of 1% phenolphthalein indicator.

Various weight ratios of extenders were tried. First, the stoichiometric amount was employed and then this amount was decreased gradually until the extender did not provide the desired molecular weight increase. The ratios of the reagents are given in Table I and the results are evaluated in the discussion.

At the end of the extension reactions, the resins obtained were cooled and dissolved in styrene to give a 65% solids solution, and cured at room temperature using 2% Methyl ethyl ketone peroxide (MEKP) and 0.25% Cobalt naphthenate (6% solution in dibutyl phthalate) and then post cured at 80°C for 3 h. Gel times were measured as the time of first gel formation at ambient temperature according to the standard ISO 2535 (2001).¹⁰

RESULTS AND DISCUSSION

Chain extension and molecular weight increase

Two different bis(2-oxazoline)s were investigated for their capacity to work as chain extenders for UPEs. In a standard polyesterification reaction, carboxylic end groups of polyesters react with hydroxyl end groups to provide the desired molecular weight polymer. During this process, the acid number of the polyester decreases continuously as the acid end groups are being used up. Commercial polyesterification reaction is usually carried on until an acid number of 30 is reached. At this point the linear unsaturated polyester usually has a molecular weight about 1500. Then the polyester is dissolved in a reactive diluent like styrene for later cross-linking. By determining the acid number and molecular weight of polyester aliquots periodically taken from an industrial reaction the relationship between these two variables were determined. This decrease in

acid number and the parallel increase in molecular weight are shown in Figure 2 for the reference polyester used in this study.

Various amounts of chain extenders were used and molecular weight increases were monitored by GPC. The lowest amount providing the desired molecular weight within a given time was chosen as optimum and these samples were studied further. Table I shows the results of stoichiometric and optimum weight ratios of extenders and the M_n values obtained during the reactions. In all cases even within 5 min, the molecular weight of the unsaturated polyester increased from 1000 to 1400. However the reaction was continued up to 30–60 min, in order to check the reversibility of reactions at 160°C. At processing temperatures as high as 250–300°C, the reaction of bis(2-oxazoline)s with carboxylic groups were known to be reversible.¹¹ However, at 160°C, in most of the runs the molecular weight of UPE continued to increase indicating further coupling reactions and no reversal.

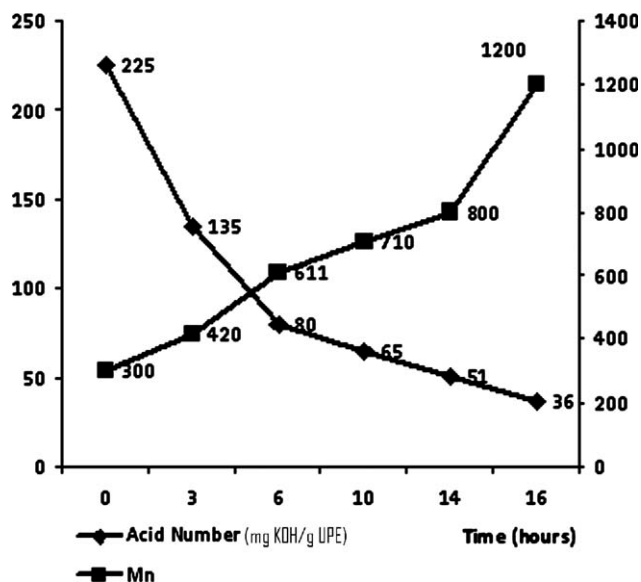


Figure 2 Acid number and M_n values during a standard commercial polyesterification.

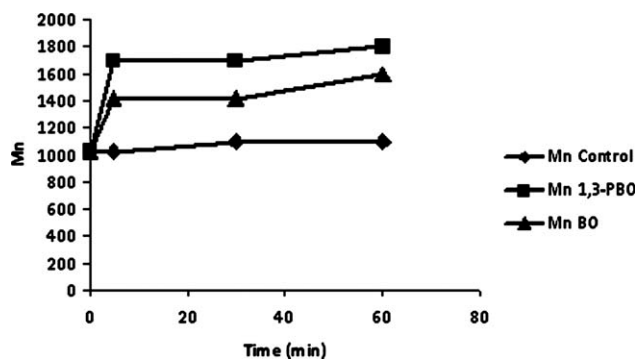


Figure 3 Molecular weight increase of UPE with 1,3-PBO and with BO.

In Table I, the results of a control (blank) run, where the short chain UPE was heated at the reaction conditions without a chain extender are also shown. In such a case, where no extender was present, the molecular weight did not increase, which proves that this polycondensation does not contribute to the molecular weight increase. During the chain extension reactions, polydispersity index values were found to increase. This was expected, because as the chain extenders are used in less than stoichiometric amounts, only some of the chains are extended while others retain their original molecular weight. Thus, chain coupling reactions are random and cause production of different length chains in the reaction medium and while the number average molecular weight increases, dispersity also increases. The observed decrease in mechanical properties is due to this increase in polydispersity index. Using initial and final molecular weights and the known initial acid number value, the acid number at the end of chain extension could be calculated. By using extenders less than the stoichiometric amounts, the acid numbers for the chain extended polyesters were about 40–50, slightly higher than the commercial

product (acid number = 30) as expected. Water absorption tests were performed on fully cured commercial polyester, PBO and BO chain extended polyesters according to ASTM D570.¹² The percent water absorption values were 0.28%, 0.33%, and 0.23%, respectively. This shows that the increase in acid number from 30 to 40–50 does not increase the water absorption of the cured samples appreciably.

The molecular weight increase of UPE caused by 1,3-PBO and BO are shown in Figure 3. When compared with Figure 2 the rapid increase in molecular weight of the polyester can be appreciated: M_n values reached 1500–1600 (the M_n value of the commercial reference) in the first few minutes when 1,3-PBO or BO were added to the reaction medium at 160°C.

At the reaction temperature of 160°C for chain extension, polycondensation did not take place; and, at or below 200°C, the ester-amide bond formed in the reaction between bis(2-oxazoline)s and carboxylic groups is known to be stable.⁸

Quarternary ammonium salts, quarternary phosphonium salts and tertiary phosphines were reported to catalyze the reaction of bis(2-oxazolines) with carboxylic groups,⁶ but in this work no catalyst was needed or used.

The poly(ester-amides) obtained following chain extension were characterized by ¹H-NMR and FTIR spectroscopy.

¹H-NMR characterization

While the initial feed composition of the monomers for the reference UPE used in this study was not disclosed by the producer, ¹H-NMR analysis presented in Figure 4 indicates the following monomers exist in the polymer: Phthalic anhydride, maleic anhydride, propylene glycol and ethylene glycol. The -CH₃ protons arising from propylene glycol appear at 1.2 ppm; -CH₂- protons of ethylene

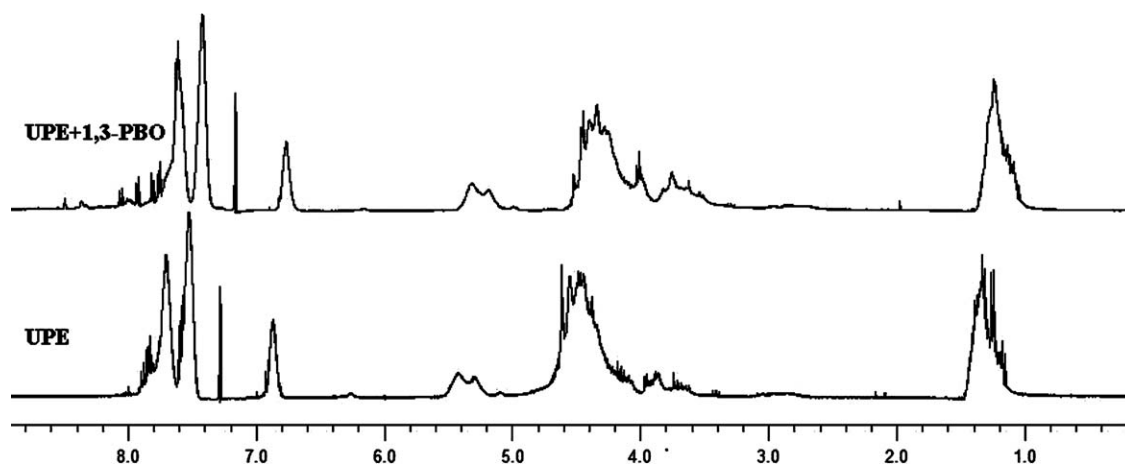


Figure 4 ¹H-NMR spectrum of 1,3-PBO chain extended UPE.



Figure 5 FTIR spectra of unmodified and chain extended UPEs.

glycol and propylene glycol at 4.4 ppm; the $-\text{CH}$ -proton of propylene glycol at 5.3 ppm; fumarate vinyl protons arising from the thermal isomerisation of maleate groups appear at 6.8 ppm and finally the phthalate aryl protons at about 7 ppm in the aromatic region.

Bis(2-Oxazoline)s show characteristic peaks at 3.9 and 4.3 ppm arising from protons on the oxazoline carbons alpha to oxygen and nitrogen. Following chain extension with bis(2-oxazoline)s, these peaks originating from the methylene groups between amide and ester bonds were identified in the $^1\text{H-NMR}$ spectrum of the chain extended UPE. When consid-

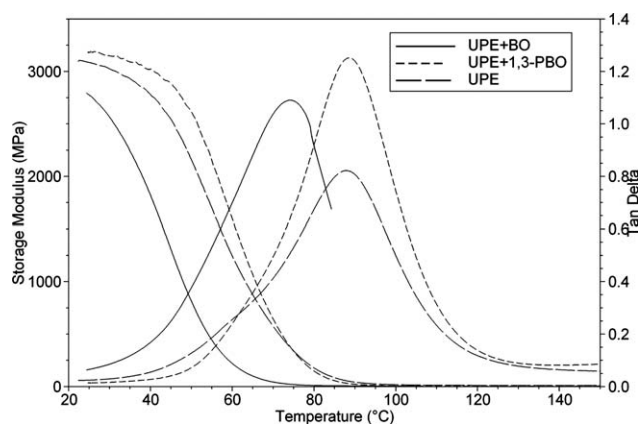


Figure 6 Tan delta and storage modulus curves of commercial and chain extended polyesters at 25°C.

ered together with rapid molecular weight increase, this $^1\text{H-NMR}$ signal is an indication of chain extension. An example spectrum of UPE extended with 3% 1,3-PBO is also shown in Figure 4.

FTIR characterization

The chain extended unsaturated polyesters were also identified by FTIR. In case of chain extension, a new amide bond was introduced to the polyester chain. This amide stretch was detected at 1540 and 1785 cm^{-1} . This region of the IR spectrum is illustrated in Figure 5 for unmodified UPE and 3% 1,3-PBO chain extended UPE.

Styrene solubility and gel time

For industrial applications it is important that the chain extended UPEs exhibit the same styrene solubilities and gel times as commercial UPEs. Therefore in each case, styrene solubility and gel time were compared with a commercial reference product. Following the chain extension the polyesters were dissolved in styrene to give a clear viscous solution containing 35% styrene. The solubilities and viscosities were found to be the same as the reference polyester. Gel times for chain extended polyesters were measured as 8–9 min, which is the same as the reference polyester. The measured gel times are given in Table II.

TABLE II
Final M_n , T_g , Storage Modulus, TGA Data and Gel Times of Commercial and Chain Extended Polyesters

UPE	Final M_n	T_g (°C)	Storage modulus (MPa)	Temperature at 5% weight loss (°C)	Gel time (min)
Commercial UPE	1500	88	3000	278	10–12
Extended with % 3 1,3-PBO	1500	88	3200	245	9–10
Extended with 4 % BO	1470	75	2875	231	8–9

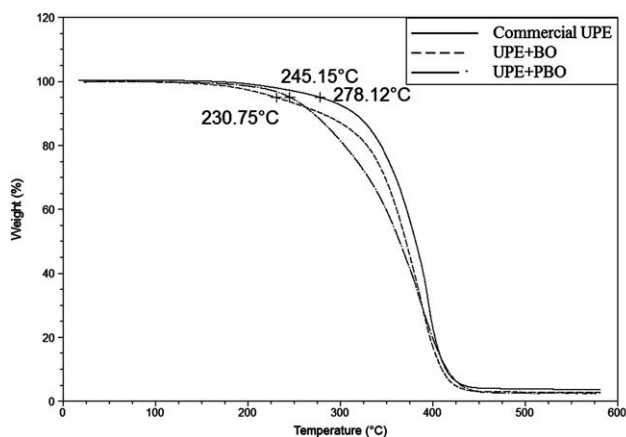


Figure 7 TGA thermograms of commercial and chain extended polyesters (Temperature at 5% weight loss).

Mechanical and thermal characterization

The chain extended and cured polyesters were examined further for their thermal and mechanical behavior. Bisoxazoline chain extenders introduce new amide linkages to the polymer chain, which would be expected to increase the T_g of the cured polyester. The commercial reference polyester cured using 2% MEKP and 0.25% Cobalt naphthenate (6% solution in dibutyl phthalate) at RT and postcured at 80°C for 3 h has a T_g of 88°C as determined by the maximum of tan delta curve and a storage modulus of 3000 MPa as determined by DMA analysis.

3% 1,3-PBO extended polyester cured under the same conditions exhibited a T_g at 88°C and a storage modulus of 3200 MPa. These values are the same or better than those of commercial polyester. In case of BO chain extension a T_g of 75°C and a storage modulus of 2875 MPa were found. The higher values obtained with 1,3-PBO is attributed to the rigidity introduced by the phenyl ring. The tan delta and storage modulus curves of all the polyesters are shown in Figure 6, and the values are listed in Table II.

Thermal stability tests were also performed for the chain extended polyesters and the reference product. The results are shown in Figure 7. The final number average molecular weight, glass transition temperature, storage modulus, and TGA values are summarized for comparison in Table II.

TGA results of the chain extended polyesters show that the temperatures corresponding to 5% weight loss are around 250°C. This value is 278°C for commercial UPE. The difference reflects the lower thermal stability¹³ of the amide linkage introduced compared to the ester linkage. However, this small decrease in thermal stability should not be detrimental in practice as unsaturated polyesters usually are not used in high temperature applications. Bisoxazoline extended unsaturated polyesters exhibit

thermal and mechanical properties that are perfectly suitable for industrial use.

CONCLUSION

Bisoxazolines were found to be effective in chain extension for unsaturated polyesters. The molecular weight of unsaturated polyesters reached the desired value of 1500 within 5–30 min when these extenders were added to the polyesterification medium at the 6th hour of an industrial production in amounts as low as 3–4% at 160°C. Solubilities, gel times, and mechanical and thermal properties of the chain extended polyesters were found to be very similar to a standard commercial product. In addition, no discernible alterations in appearance and color were observed.

With the help of this chain extension the diol loss due to evaporation that is usually encountered in the late stages of commercial UPE manufacture will be eliminated, giving economies in raw material and minimizing pollution. When thought in terms of industrial production, the benefits brought on by the extenders such as shortened reaction time, reduced energy use, and increased yield present a major advantage. Starting with short chain polyesters of molecular weight about 1000, and continuing the polycondensation reaction to a molecular weight above 1500, would result in a 2% weight loss due to the water that needs to be separated. This can be easily calculated from the decrease in acid number. The actual loss in practice is probably much higher due to the azeotropic loss of diols along with water. Using the chain extension method described in this work there is a 3–4% increase in the weight of the product. The total increase in polymer yield is therefore at least 5–6% which is an attractive number for a UPE producer and the price gain would offset the price of the extender that needs to be used. The reduction in labor and energy costs when the overall reaction time is reduced from 20 h to 6–7 h will depend on the actual scale of the reaction and the design of the reactor.

Therefore it is concluded that, the use of these extenders decreases the production time and increases the yield of the polyester substantially, without altering styrene solubility and gel time of the polyester.

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References

1. Scheirs, J.; Long, T. E. *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters, Unsaturated Polyesters, Part VII*, 709 ed; Wiley: Hoboken, 2003; p 699.

2. De Oliveira, A. B.; Jorge, I. F.; Suarez, A. Z.; De S Basso, N. R.; Einloft, S. *Polym Bull* 2000, 45, 341.
3. Loontjens, T.; Pauwels, K.; Derks, F.; Neilen, M.; Sham, C. K.; Serne, M. *J Appl Polym Sci*, 2009, 65, 1813.
4. Taylan, E.; Küsefoğlu, S. H. *J Appl Polym Sci* 2009, 112, 1184.
5. Taylan, E.; Küsefoğlu, S. H.; *J Appl Polym Sci*, 2011, 119, 1102.
6. Haralabakopoulos, A. A.; Tsiourvas, D.; Paleos, C. M. *J Appl Polym Sci* 1999, 71, 2121.
7. Nascimento, C. R.; Azuma, C.; Bretas, R.; Farah, M.; Dias, L. M. *J Appl Polym Sci* 2009, 115, 3177.
8. Po, R.; Abis, L.; Fiocca, L.; Mansani, R. *Macromolecules* 1995, 28, 5699.
9. ASTM Standard Test Method for Neutralization Number by Color-Indicator Titration, "ASTM D 974-64", *Annual Book of ASTM Standards*, 1973, 412-415.
10. ISO 2535: Measurement of Gel Time at Ambient Temperature; International Organization for Standardization: Geneva, 2001.
11. Loontjens, T.; Pauwels, K.; Derks, F.; Neilen, M.; Sham, C. K.; Serne, M.; *J Appl Polym Sci* 1997, 65, 1813.
12. ASTM Standard Test Method for Water Absorption of Plastics, "ASTM D570", 2010, 98(2010) e1.
13. Inata, H.; Matsumura, S. *J Appl Polym Sci* 1987, 33, 3069.