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Synthesis, characterization and photopolymerization of vinyl functionalized poly (ε-caprolactone)

S. S. Liow[*1], *L. K. Widjaja*[1], *V. T. Lipik*[1], *M. J. M. Abadie*[1,2]

[1]School of Materials Science & Engineering, MSE/NTU, Block N4.1, 50 Nanyang Avenue, Nanyang Technological University, Singapore 639798, Singapore
[2]Laboratory of Polymer Science and Advanced Organic Materials, LEMP/MAO, Université Montpellier 2, S.T.L., Place Bataillon, 34095 Montpellier Cedex 05, France

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Abstract. Vinyl functionalized poly (ε-caprolactone) with molar mass ranging from 500–5000 Da were synthesized by ring opening polymerization and further photopolymerized. One-step synthesis and functionalization is achieved based on ring opening polymerization (ROP). Hydroxyl butyl vinyl ether (HBVE) was employed to play the role as the initiator of ROP, and photo-curable functional group. The presence of CH_2=CH peak in Fourier Transform Infrared (FTIR) spectra confirmed that vinyl end groups were successfully attached to poly (ε-caprolactone) (PCL) macromolecule. Kinetic parameters of cationic photopolymerization of vinyl functionalized PCL were investigated. The activation energy was estimated at 11.33 kJ/mol, by assuming the cationic system followed second-order autocatalytic model.

Keywords: *tailor-made polymers, poly (ε-caprolactone), cationic photopolymerization, functionalization; curing kinetics*

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1. Introduction

Aliphatic polyesters, such as Polyglycolide (PGA), Polylactide (PLA), Poly (ε-caprolactone) (PCL) and their copolymers have received great interest in biomedical applications due to their good biocompatibility [1] and bioabsorbability. They degrade mainly by hydrolysis of ester linkages, yield hydroxyl carboxylic acids, which in most cases are ultimately metabolized [2]. The functionalization of oligomers such as ε-caprolactone, with unsaturated groups and subsequent Ultraviolet (UV) curing [3, 4] or polymerization [5, 6] has been studied. Especially, UV curing is interesting since it usually provides fast, well-controlled and low energy consumption process, capable of forming thin films or predefined patterns, and can be carried out at low temperatures [7]. Our research focuses on the development of novel controlled drug release system based on mono-functionalized polyesters/ copolyesters and successive cationic UV grafting to yield fully or partially bioabsorbable therapeutic multilayered surface coatings, with variable rate of degradation. If this polyester/ copolyester is multifunctionalized, consequent UV crosslinking can yield fully bioabsorbable polymeric network, which is suitable for biomedical applications such as tissue engineering scaffolds, cell encapsulations and short term drug delivery vehicles.

To prepare polymers with variable rates of degradation, most studies have focused on copolymerization [8–11]. Copolymerization allows blending of two or more polymers, in order to achieve variable degradation patterns. In-depth research of degradation behaviors of the copolymers in different compositions and prolonged synthesis procedure are expected. It could be more convenient, if the vari-

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[*]Corresponding author, e-mail: Liow0019@ntu.edu.sg
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able rate of degradation is obtained by formation of multilayered polymeric coatings, by rapid and well-controlled UV curing.

Photo-curable functional groups, such as methacrylates have been used most often as unsaturated group attached on precursor oligomers [4–6]. Functionalization with coumarin and phenylazide has been reported as well [12, 13]. In these cases, free radical photopolymerization was employed. When cured radically, these photoreactive functions are subjected to oxygen and impurities inhibition, which could lead to incomplete conversion. Immune inflammation reaction was reported to be related to the leach out of monomers or unreacted oligomers from polymeric implants. Another anticipated risk of acrylates is a higher level of skin sensitization as compared to most vinyl ethers [14]. In addition, the synthesis of acrylates, coumarin and phenylazide functionalized precursor oligomers usually involved two-steps reaction: precursor oligomers synthesis and subsequent functionalization. Longer preparation time and tedious purification are expected.

To overcome these problems, we are investigating an alternative UV curing method – cationic photopolymerization, where mono-functionalized oligocaprolactone was used as precursor oligomers. The main advantage of cationic photopolymerization is that it is not inhibited by oxygen and capable of 'dark curing'. Synthesis and functionalization can be achieved in one step, by using ROP. HBVE was employed to play the role as the initiator of ROP, and photo-curable functional group. Most vinyl ethers are expected to have a lower level of skin sensitization as compared to acrylates.

In this study, we report the feasibility to photopolymerize precursor oligomers. The kinetics of cationic photopolymerization of HBVE functionalized PCL (vinyl-PCL) will be discussed.

2. Materials and methods

2.1. Materials

Epsilon-caprolactone monomer (99%) was purchased from Fluka, Singapore and used without further purification. The initiator 4-hydroxybutyl vinyl ether (stabilized with 0.01% KOH) (HBVE) was obtained from BASF, Canada. Tin (II) 2-ethylhexanoate ($SnOct_2$) was purchased from Sigma, Singapore. Toluene was purified by distillation. Chloroform, methanol and dimethyl sulfoxide (DMSO) were of analytical grade and used as received. The photoinitiator: bis [4(diphenylsulfonio)-phenyl] sulfide-bis-hexafluoroantimonate 50% solution in propylene carbonate supplied as Cyracure® UVI 6976 by Union Carbide (USA) was used without further purification.

2.2. ROP and functionalization of vinyl-PCL

To functionalize PCL of 2000 g/mol, 5 mmol of HBVE as initiator, 0.5 mmol of $SnOct_2$ as catalyst and 25 ml of freshly distilled toluene were charged into a 50 ml three neck flask. The flask was evacuated by vacuum, and purged with nitrogen before being placed into an oil bath, at 80°C. After 30 minutes, 10 g of ε-caprolactone monomer was charged into the reaction flask. The reaction was kept at 110°C for 24 h. The crude products were dissolved in chloroform and precipitated in a fourfold excess of methanol. The polymer was dried at 40°C under vacuum for 24 h.

2.3. Measurements

The molar weights (number average molar weight M_n and weight average molar weight M_w) and polydispersity index (PDI) were determined by Size Exclusion Chromatograph (SEC) (Agilent GPC 1100 series), using monodisperse polystyrene standard for calibration. Measurements were made at room temperature with chloroform as solvent (1 ml: 1 mg). Matrix Assisted Laser Desorption/Ionization-Time Of Flight (MALDI-TOF) mass spectrometry was performed on Shimadzu Biotech (Axima-ToF^2) in linear mode. MALDI-TOF mass-spectra were acquired by averaging at least 100 laser shots. 2,5-dihydroxyl benzoic acid was used as matrix and tetrahydrofuran as solvent. Sodium chloride was dissolved in methanol and used as the ionizing agent. Samples were prepared by mixing 20 µl of polymer solution in tetrahydrofuran (2 mg/ml) with 20 µl of matrix solution (10 mg/ml) and 1 µl of a solution of ionizing agent (1 mg/ml). Then 1 ml of these mixtures was deposited on a target plate and allowed to dry in air at room temperature. Calibration was made with polyethylene glycol 10 kDalton. Nuclear magnetic resonances based on proton (^{1}H NMR) spectra were recorded in $CDCl_3$ on a Bruker 400 MHz Spectrometer.

Glass and melt transition temperatures were determined by Differential Scanning Calorimetry (TA Instruments Q10-0095). The measurements were carried out from –90 to 120°C at heating rate of 10°C/min. Functional end groups were determined by Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer FTIR Spectrum GX spectrometer), using powdered potassium bromide (KBr) as matrix.

2.4. Photopolymerization of vinyl-PCL

Differential Scanning PhotoCalorimetry (DPC) (TA Instruments MDSC-2920 equipped with a photocalorimetric accessory) was used to investigate the kinetics of cationic photopolymerization of vinyl group present in monofunctional PCL 0.5, 2 and 5 kDa. Pulverized vinyl-PCL was dissolved in two solvents; non-photoreactive DMSO and photoreactive HBVE respectively. The composition is tabulated in Table 1.

The initiation light source was a 200 W high-pressure mercury lamp, which gave a UV light intensity over wavelength range of 200–440 nm. 3.0 mg of samples were placed in aluminum standard pans covered with a disc of polyethyleneterephthalate (PET) foil to maintain equal distribution of solution layer under investigation. The samples were exposed to UV light of intensity in the range of 25 mW/cm^2, for 5 minutes. Also, samples were subjected to 1 minute isothermal treatment prior to and after the UV exposure, to ensure constant temperature. A nitrogen flux of 50 cm^3/min assured homogeneity of temperature in the measuring cell.

2.4.1. Calculations

The degree of conversion (α) can be obtained from the DPC exotherm as shown in Equation (1):

$$\alpha = \frac{\Delta H_{\text{exp}}}{\Delta H_0} \tag{1}$$

and the theoretical enthalpy at full conversion of vinyl double bonds (ΔH_0) is determined by Equation (2):

$$\Delta H_0 = f\left(\frac{\Delta H_{Tf}}{m}\right) \tag{2}$$

where f is the functionality; ΔH_{Tf} is the theoretical enthalpy of vinyl ether function, 14.3 kcal/mol [15] and m is the molar weight of each macromolecule. List of theoretical enthalpy used in this study is calculated using Equation (2) and tabulated in Table 2. As an example for the HBVE functionalized PCL (M_n 2000 Da) in DMSO solution (80/20), the theoretical enthalpy is given by Equation (3):

$$\Delta H_0 = 1\cdot 0.8\left(\frac{14300\cdot 4.1839}{2000+116}\right) = 22.62\left[\frac{\text{J}}{\text{g}}\right] \tag{3}$$

The autocatalytic model as shown in Equation (4) was used to calculate the kinetic parameters. Autocatalytic model assumes that in a curing process, the measured heat flow is proportional to the conversion rate (dα/dt). This assumption is valid if the testing material exhibiting single reaction without any other enthalpic events, such as evaporation of solvent or significant changes in heat capacity with conversion [16] (Equation (4)):

$$\frac{\mathrm{d}\alpha_{(t,T)}}{\mathrm{d}t} = k_{(T)}\alpha^m(1-\alpha)^n \tag{4}$$

where dα/dt, the reaction rate [min^{-1}]; α, the fractional conversion after time t; $k_{(T)}$, temperature dependent rate coefficient [min^{-1}]; n, m, reaction orders of propagation and initiation respectively. Second-order autocatalytic model was assumed by fixing ($m + n = 2$).Temperature dependent rate coefficient $k_{(T)}$ is assumed to follow the Arrhenius equation (Equation (5)):

Table 2. Theoretical enthalpies (ΔH_0) at full conversion calculated from Equation (2)

Compound	Theoretical enthalpy ΔH_0 [J/g]
PCL 2k DMSO 80/20	22.62
PCL 2k HBVE 50/50	272.03
PCL Neat Resin HBVE 50/50	257.89

Table 1. Compositions of vinyl-PCL with non-photoreactive and photoreactive solvent

Compound	PCL [wt%]	Solvent [wt%]	Photo reactive solvent	Initiator UVI 6976 [wt%]
PCL 2k/DMSO	80	20	No	4
PCL 2k/HBVE	50	50	Yes	4

$$k_{(T)} = Ae^{-\frac{E_a}{RT}} \tag{5}$$

where E_a is the activation energy, A is the frequency factor, R is the ideal gas constant and T is the absolute temperature [K].

3. Results and discussion

In the preliminary experiments, we functionalized PCL by using HBVE in the presence of $SnOct_2$. The resulting vinyl-PCL was characterized by its molar weights, functional end groups and transition temperatures, using several techniques including SEC, MALDI-TOF, FTIR and Differential Scanning Calorimetry (DSC). Linearly grafted polymer was obtained by photopolymerization of vinyl-PCL under UV exposure.

3.1. ROP and functionalization of vinyl-PCL

ROP of cyclic ester makes it possible to prepare polyesters with defined molar weights, low polydispersity index, and functionalized end groups, due to the absence or very limited side reactions and by products [2]. To enable photo curing of PCL, monofunctional vinyl ether, in this case is HBVE, was incorporated into each PCL chain. Targeted molar weight was calculated using Equation (6):

$$DP = \frac{MW_{targeted}}{m_{monomer}} = \frac{[M]}{x[I]} \tag{6}$$

where DP is the degree of polymerization, $m_{monomer}$, molar weight of caprolactone monomer; $[M]$, monomer concentration; x, functionality of initiator (in this case $x = 1$ since monofuctional HBVE was used as initiator); $[I]$, initiator concentration. Figure 1 shows the reaction scheme.

In ROP of PCL, we used HBVE as initiator, and $SnOct_2$ as catalyst. $SnOct_2$ is now widely used as catalyst of degradable polymer synthesis because stannous salts have been approved for pharmaceutical applications [17]. The main mechanisms of $SnOct_2$ catalyzed ROP proposed in literatures [18, 19] are shown in Figure 2.

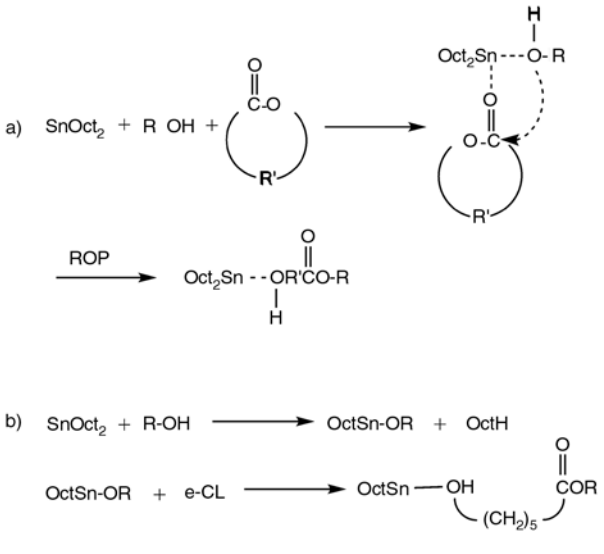

Figure 2. The main ROP mechanism proposals with $SnOct_2$ as catalyst, a) complexation of a monomer and alcohol prior to ROP [18] and b) formation of a tin-alkoxide before ROP of ε-CL [19]

PCL with wide range of molar weights ranging from 0.5–40 kDa were successfully synthesized but only low molar weights PCL (0.5, 2 and 5 kDa) were used for further photo grafting. In this study, we defined low molar weight PCL as oligomer hav-

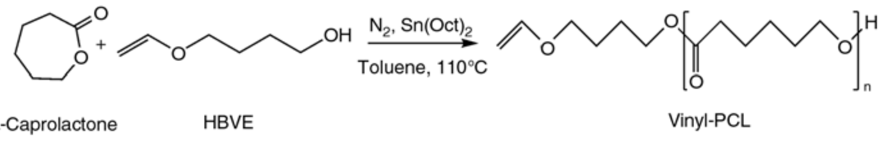

Figure 1. Reaction scheme for ROP of vinyl-PCL using HBVE as initiator, and $SnOct_2$ as catalyst

Table 3. Molecular mass and melting transition temperatures of vinyl-PCL prepolymer

		SEC			¹H NMR	MALDI-TOF	
Target M_n [kDa]	**[HBVE]/ [$SnOct_2$]**	**M_n [g/mol]**	**M_w [g/mol]**	**Poly Dispersity Index (PDI)**	**M_n [g/mol]**	**M_n [g/mol]**	**T_m [°C]**
0.5	2	1898	3502	1.84	3609	612	40.29
2	2	7091	11189	1.57	3995	1011	57.69
5	10	4574	10051	2.20	4643	ND[a]	58.28

[a]ND – not detected

ing molar weight from 500–5000 Da. An overview of the properties of vinyl-PCL is presented in Table 3.

For PCL 5 kDa both molar weights obtained from SEC and NMR showed consistency with one another. Note that the experimental M_n follows closely to targeted value when molar ratio of HBVE/SnOct$_2$ is 10. It is observed in the PCL 0.5 kDa and PCL 2 kDa that M_n (detected by SEC and NMR) is higher than targeted value when molar ratio of HBVE/SnOct$_2$ was decreased to 2, where amount of SnOct$_2$ increased. In the presence of ROH (in our case is HBVE), if the proportion [ROH]/ [SnOct$_2$] does not exceed approximately 2, ROH acts mostly as a co-initiator, reacting with SnOct$_2$ [19]. The increased amount of SnOct$_2$ has probably initiated some macromolecules. This explained why M_n tends to be higher when [ROH]/[SnOct$_2$] ratio is 2. Above this ratio, ROH retains its function as an initiating compound [19].

PDI (M_w/M_n ratio) observed in all synthesized PCL were high. In the case of PCL 5 kDa, this could result from bimolecular transesterification in presence of SnOct$_2$, not shifting M_n but M_w [19]. SnOct$_2$ is well known for causing transesterification reactions at elevated temperatures [2]. For PCL 5 kDa, only MALDI spectra for low molar mass fraction were detected because of high PDI. Sometimes, the MALDI results are completely out of range for polymer with high PDI [20].

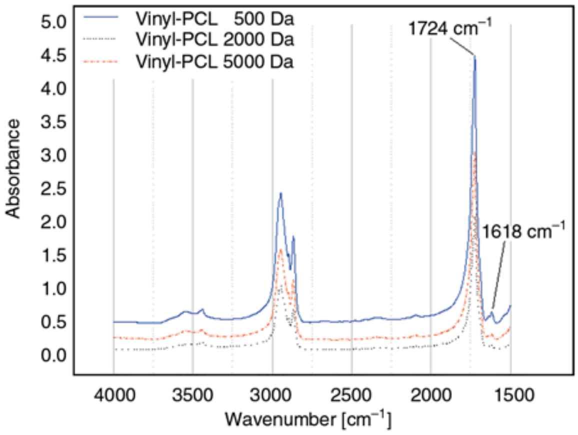

Figure 3. FTIR spectra of 0.5, 2 and 5 kDa vinyl-PCL

3.2. End group analysis by FTIR

It is known that vinyl ether is a function involved in cationic photopolymerization. From Figure 3, the low intensity peak at 1618 cm^{-1} corresponds to the vibration of the vinyl CH$_2$=CH double bonds, and the strong peak at 1725 cm^{-1} indicates vibration of abundant C=O ester bonds in PCL. This result shows that the vinyl group is successfully linked to PCL after ring opening polymerization.

3.3. Photopolymerization of vinyl-PCL

Before photopolymerization, two sets of samples were prepared by dissolving vinyl-PCL in DMSO and HBVE respectively. Upon UV exposure, polymerization of double bonds leads to formation of linearly grafted vinyl-PCL as shown in Figure 4 and Figure 5.

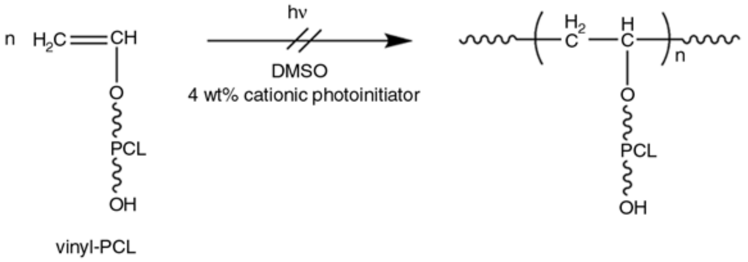

Figure 4. Typical photopolymerization reaction of vinyl-PCL in non-photo reactive solvent (DMSO)

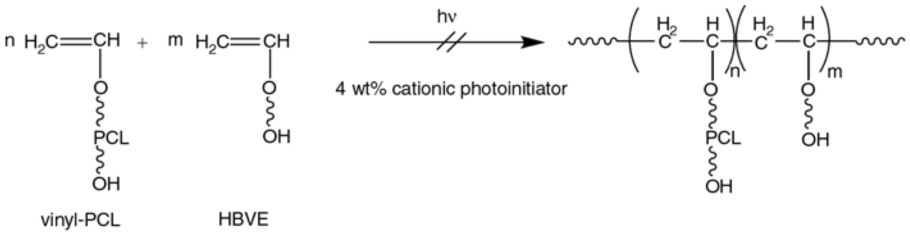

Figure 5. Typical photopolymerization reaction of vinyl-PCL in photo reactive solvent (HBVE)

3.3.1. Photopolymerization in non-photo reactive solvent (DMSO)

Photocuring of the vinyl-PCL in DMSO in presence of cationic photoinitiator (Cyracure® UVI 6976) has been performed. Figure 6 shows typical DPC exotherm plot of PCL 2 kDa photopolymerized in non-reactive solvent (DMSO), initiated by UVI 6976. The total area under the curve corresponds to the polymerization enthalpy (ΔH_{exp}) of the sample. Broad peak is obtained indicating low reactivity of the photopolymerization system. Low reactivity of the system is further presented by long induction time and low rate coefficients (k), as compared to HBVE system. It is in fact reasonable since the photo reactive species (vinyl double bonds) is only a small portion in a long macromer.

From the plot of heat flow over time, one can obtain information such as induction time (time of 1% monomer conversion), polymerization enthalpy, percentage of conversion and reaction rate coefficient (k), as shown in Table 4. Conversion was calculated from Equation (1). Average conversions range from 73–97% within 5 minutes of UV exposure.

On the other hand, note that cationic photopolymerization continues curing long after exposure once initiated [21, 22]. This is termed as 'dark curing'. Therefore, conversion of vinyl double bonds is expected to continue further until complete conversion after exposure. In addition, cationic photopolymerization is not inhibited by traces of oxygen in the air or radical impurities but inhibiting and retarding effects or chain transfer reactions were observed with bases, water, alcohols [23].

In cationic polymerization, the reaction rate coefficient (k) is affected by the nature of counter ion [24]. Lazauskaité and coworkers have examined the kinetic parameters of cationic photopolymerization of epoxies monomer initiated by photoinitiator having the same counter ions in this study [25]. At 60°C, both k values are consistent with each other. The reaction rate coefficient (k) is assumed to follow Arrhenius equation (Equation (4)). An estimation of activation energy (E_a) was obtained as 11.33 kJ/mol by fitting a linear relationship of ln$k$ and reciprocal of temperature, as shown in Figure 7. Estimation of activation energy is considered low as compared to vinyl ether function alone (14.3 kcal/mol = 59.83 kJ/mol) [15]. Lower activa-

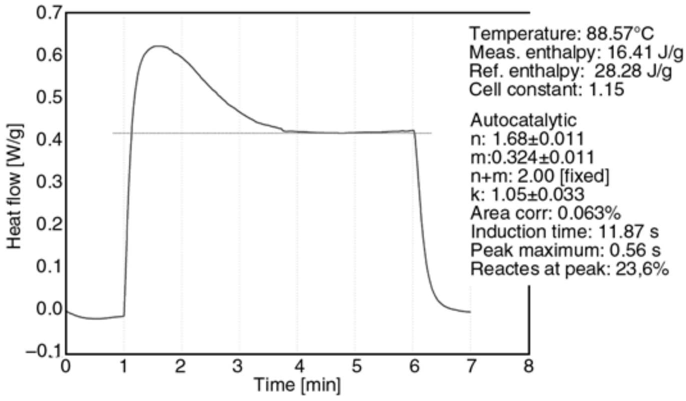

Figure 6. Typical DSC exotherm of vinyl-PCL 2 kDa in DMSO solution at 90°C. Exothermic peak is pointing upwards.

Table 4. Kinetic parameters of the second-order autocatalytic model for the photopolymerization of vinyl-PCL in DMSO solution with 4 wt% UVI 6976 obtained by TA specialty library analysis

Temperature of experiment [°C]	Enthalpy, ΔH_{exp} [J/g]	Peak maximum [s]	Induction time [s]	Reacted at peak [%]	Rate coefficient, k [min^{-1}]	m	Conversion^{b}
58.9	21.9	0.47	11.2	14.0	2.20	0.637	0.967
68.8	21.4	0.49	11.7	16.2	2.48	0.623	0.947
78.6	18.4	0.50	10.7	18.4	2.65	0.625	0.815
88.6	16.5	0.55	10.6	25.0	3.44	0.683	0.728
98.4	17.1	0.67	10.9	30.5	3.23	0.706	0.755

E_a= 11.33 ± 2.44 kJ/mol, R^2: 0.88

Frequency factor, A: 133.75

^{b}Conversion within 5 minutes of UV exposure was calculated using Equation (1)

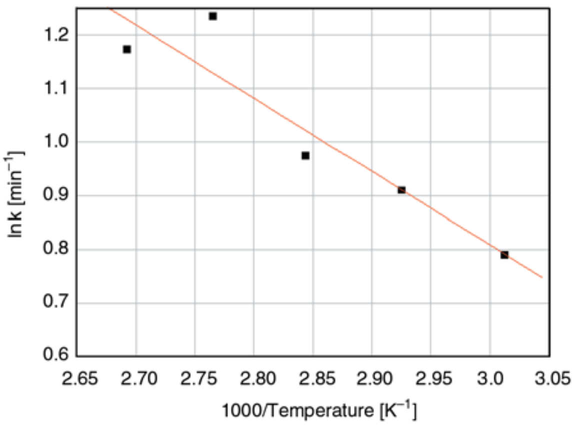

Figure 7. ln*k* vs. 1/*T* Arrhenius plot

tion energy indicates a higher reactivity system. But, vinyl-PCL oligomeric system could not be more easily polymerized than the vinyl ether monomer.

Unlike monomeric system studied by Lazauskaité, oligomeric system has lower diffusivity of active centers than monomeric system, it is necessary to take into account the diffusion controlled reaction. According to Rabinowitch [26] the overall reaction rate coefficient, ke, can be expressed as Equation (7):

$$\frac{1}{k_e}=\frac{1}{k_{chem}}+\frac{1}{k_{diff}} \qquad (7)$$

where k_{chem} is the chemically controlled and k_{diff} is the diffusion controlled rate coefficient, and k_{chem} follows an Arrhenius temperature dependence. System with low diffusivity can decrease the overall rate coefficient significantly, and thus affect temperature dependence, resulting in low activation energy estimation.

3.3.2. Photopolymerization in photoreactive solvent (HBVE)

Photocuring of the vinyl-PCL in HBVE in presence of cationic photoinitiator (Cyracure® UVI 6976) has been performed. Photopolymerization in HBVE follows the reaction scheme presented in Figure 5. Since HBVE is photoreactive, it is expected to receive enthalpy contributed by polymerization of HBVE double bonds in addition to vinyl-PCL double bonds. Figure 8 shows a typical exothermic plot of this system. Sharper peak is obtained as compared to DMSO system, indicating higher reactivity of the photopolymerization system. High reactivity of the system is further presented by the lower induction time and higher rate coefficients (*k*), as compared to DMSO system in Table 4. It is expected since both double bonds from HBVE monomers and vinyl-PCL were participating in photopolymerization.

The kinetic results of vinyl-PCL in HBVE solution is compared with neat resin system in HBVE solution initiated by the same initiator, as shown in Table 5. Average enthalpy of vinyl-PCL is higher than the neat resin system. It is expected that the difference in enthalpy is contributed when vinyl-PCL photopolymerized. However, the difference is too small to be conclusive. Therefore it cannot be concluded here from results in Table 5 that the double bonds in vinyl-PCL were photopolymerized successfully.

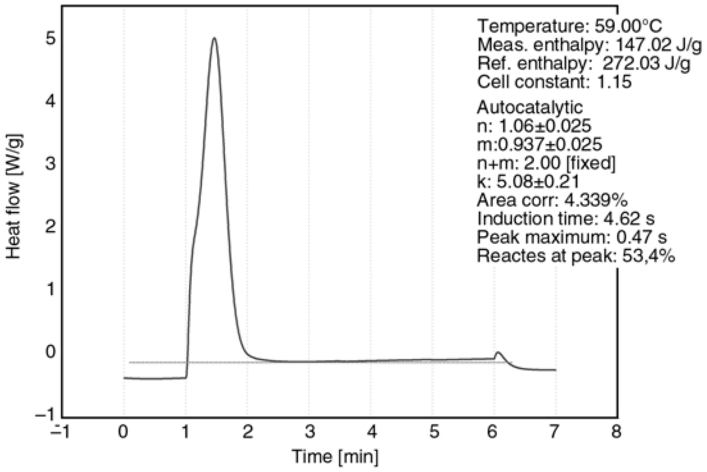

Figure 8. Typical DSC exotherm of vinyl-PCL 2 kDa in HBVE solution at 60°C. Exothermic peak is pointing upwards.

Table 5. Comparision of kinetic parameters of vinyl-PCL with PCL neat resin, both in HBVE reactive solvent at 60°C obtained by TA specialty library analysis

Compound	Enthalpy ΔH_{exp} [J/g]	Peak maximum [s]	Induction time [s]	Reacted at peak [%]	Rate coefficient k [min^{-1}]	m	Conversion[b]
PCL 2kDa HBVE 50/50	155.5 ± 11.9	0.48	4.80	0.519	6.30	0.985	0.58
PCL NR HBVE 50/50	151.2 ± 12.1	0.22	3.63	0.452	10.92	0.689	0.58

[b] Conversion within 5 minutes of UV exposure was calculated using Equation (1)

4. Conclusions

Our preliminary results have proved that cationic photopolymerization is capable of curing vinyl ether functionalized precursor oligomers with high conversion in DMSO solution. One-step synthesis and functionalization is established by using hydroxyl butyl vinyl ether as initiator and photocurable functional group. The presence of CH_2=CH peak in FTIR spectra confirmed that vinyl end groups were successfully attached to PCL macromolecule.

Photopolymerization kinetics of vinyl-PCL was studied in both DMSO and HBVE solution. Photocuring of the vinyl-PCL in DMSO in presence of cationic photoinitiator (Cyracure® UVI 6976) yield polymerization enthalpy of 17–22 J/g. The activation energy was calculated to be 11.33 kJ/mol, by assuming the cationic system followed autocatalytic model. In HBVE solution, it cannot be concluded that vinyl-PCL contributed to the resulted polymerization enthalpy, in the comparison to neat resin system. This is mainly due to the fact that the enthalpy contribution of vinyl-PCL is too small compare to HBVE.

References

[1] Serrano M. C., Pagani R., Vallet-Regí M., Peña J., Rámila A., Izquierdo I., Portolés M. T.: In vitro biocompatibility assessment of poly([epsilon]-caprolactone) films using L929 mouse fibroblasts. Biomaterials, **25**, 5603–5611 (2004).
DOI: 10.1016/j.biomaterials.2004.01.037

[2] Albertsson A. C.: Degradable aliphatic polyesters. Springer, Berlin/Heidelberg (2002).

[3] Grijpma D. W., Hou Q., Feijen J.: Preparation of biodegradable networks by photo-crosslinking lactide, ε-caprolactone and trimethylene carbonate-based oligomers functionalized with fumaric acid monoethyl ester. Biomaterials, **26**, 2795–2802 (2005).
DOI: 10.1016/j.biomaterials.2004.08.002

[4] Sawhney A. S., Pathak C. P., Hubbell J. A.: Bioerodible hydrogels based on photopolymerized poly(ethylene glycol)-co-poly(α-hydroxy acid) diacrylate macromers. Macromolecules, **26**, 581–587 (1993).
DOI: 10.1021/ma00056a005

[5] Storey R. F., Warren S. C., Allison C. J., Wiggins J. S., Puckett A. D.: Synthesis of bioabsorbable networks from methacrylate-endcapped polyesters. Polymer, **34**, 4365–4372 (1993).
DOI: 10.1016/0032-3861(93)90203-M

[6] Helminen A. O., Korhonen H., Seppala J. V.: Crosslinked poly (ε-caprolactone/D,L-lactide) copolymers with elastic properties. Macromolecular Chemistry and Physics, **203**, 2630–2639 (2002).
DOI: 10.1002/macp.200290039

[7] Schwalm R.: UV Coatings: Basics, recent developments and new applications. Elsevier, Amsterdam (2007).

[8] Hakkarainen M., Albertsson A-C., Karlsson S.: Weight losses and molecular weight changes correlated with the evolution of hydroxyacids in simulated *in vivo* degradation of homo- and copolymers of PLA and PGA. Polymer Degradation and Stability, **52**, 283–291 (1996).
DOI: 10.1016/0141-3910(96)00009-2

[9] Dirk W., Grijpma A. J. P.: (Co)polymers of L-lactide 1. Synthesis, thermal properties and hydrolytic degradation. Macromolecular Chemistry and Physics, **195**, 1633–1647 (1994).
DOI: 10.1002/macp.1994.021950515

[10] Pitt G. G., Gratzl M. M., Kimmel G. L., Surles J., Sohindler A.: Aliphatic polyesters II. The degradation of poly (DL-lactide), poly (ε-caprolactone), and their copolymers *in vivo*. Biomaterials, **2**, 215–220 (1981).
DOI: 10.1016/0142-9612(81)90060-0

[11] Iojoiu C., Cade D., Fessi H., Hamaide T.: Synthesis of oligocaprolactone vinyl ether macromonomers and their use for indomethacin encapsulation in polymer nanoparticles based on polycaprolactone macromonomer-maleic anhydride-*N*-vinyl pyrrolidone terpolymers. Polymer International, **55**, 222–228 (2006).
DOI: 10.1002/pi.1964

[12] Matsuda T., Mizutani M., Arnold S. C.: Molecular design of photocurable liquid biodegradable copolymers. 1. Synthesis and photocuring characteristics. Macromolecules, **33**, 795–800 (2000).
DOI: 10.1021/ma991404i

[13] Mizutani M., Arnold S. C., Matsuda T.: Liquid, phenylazide-end-capped copolymers of ε-caprolactone and trimethylene carbonate: Preparation, photocuring characteristics, and surface layering. Biomacromolecules, **3**, 668–675 (2002).
DOI: 10.1021/bm0101670

[14] Blyler Jr. L. L., Paczkowski M. A., Simoff D. A., Varlemann U., Wang N. P.: Vinyl ether terminated oligomers and polymers. U.S. Patent 5989627, USA (1999).

[15] Hoyle C. E.: Calorimetric analysis of photopolymerization. in 'Radiation curing: Science and technology' (ed.: Pappas S. P.) Plenum Press, New York, 57–133 (1992).

[16] Cho J-D., Hong J-W.: Curing kinetics of UV-initiated cationic photopolymerization of divinyl ether photosensitized by thioxanthone. Journal of Applied Polymer Science, **97**, 1345–1351 (2005).
DOI: 10.1002/app.21838

[17] Wu X. S.: Synthesis and properties of biodegradable lactic/glycolic acid polymers. in 'Encyclopedic handbook of biomaterials and bioengineering' (ed.: Wise D. L.) 1015–1054 (1995).

[18] Kricheldorf H. R., Kreiser-Saunders I., Stricker A.: Polylactones 48. $SnOct_2$-initiated polymerizations of lactide: A mechanistic study. Macromolecules, **33**, 702–709 (2000).
DOI: 10.1021/ma991181w

[19] Kowalski A., Duda A., Penczek S.: Kinetics and mechanism of cyclic esters polymerization initiated with tin (II) octoate, 1: Polymerization of ε-caprolactone. Macromolecular Rapid Communications, **19**, 567–572 (1998).
DOI: 10.1002/(SICI)1521-3927(19981101)19:11<567::AID-MARC567>3.0.CO;2-T

[20] Pasch H., Schrepp W.: MALDI-TOF mass spectrometry of synthetic polymers. Springer, Berlin (2003).
DOI: 10.1007/s00216-004-3038-7

[21] Abadie M. J. M., Voytekunas V. Y.: New trends in UV curing. Eurasian Chemico-Technological Journal, **6**, 67–77 (2004).

[22] Decker C.: Photoinitiated crosslinking polymerisation. Progress in Polymer Science, **21**, 593–650 (1996).
DOI: 10.1016/0079-6700(95)00027-5

[23] Fouassier J-P.: Photoinitiation, photopolymerization, and photocuring: Fundamentals and applications. Hanser, Cincinnati (1995).

[24] Kim Y-M., Kris Kostanski L., MacGregor J. F.: Kinetic studies of cationic photopolymerizations of cycloaliphatic epoxide, triethyleneglycol methyl vinyl ether, and cyclohexene oxide. Polymer Engineering and Science, **45**, 1546–1555 (2005).
DOI: 10.1002/pen.20383

[25] Lazauskaité R., Budreckiené R., Grazulevicius J. V., Abadie M. J. M.: Cationic photopolymerization of 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane initiated by sulfonium salt and iron arene complex. Advanced Synthesis and Catalysis, **342**, 569–573 (2000).
DOI: 10.1002/1521-3897(200006)342:6<569::AID-PRAC569>3.0.CO;2-J

[26] Rabinowitch E.: Collision, co-ordination, diffusion and reaction velocity in condensed systems. Transactions of the Faraday Society, **33**, 1225–1233 (1937).
DOI: 10.1039/TF9373301225