Synthesis and Structure of Butylene Terephthalate-ε-Caprolactone Copolyesters

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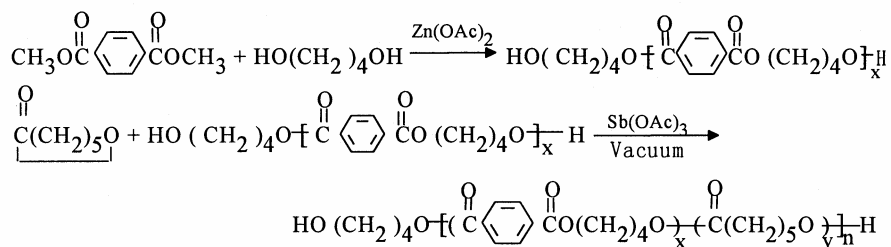
Abstract: A series of butylene terephthalate-ε-caprolactone copolyesters (BCL) with different hard segment content were successfully synthesized and characterized by ^{1}H-NMR, DSC, PLM and U-viscometer. The sequence structure and crystallization characteristics of BCL copolyesters were carefully investigated.

Keywords: BCL copolyesters, polycondensation, hard segment, soft segment, sequence structure, crystallization behavior, spherulite morphology.

Butylene terephthalate-ε-caprolactone copolyesters (BCL) are $(AB)_n$ type segmented copolymers exhibiting a two-phase structure with the hard domains as physical crosslinks for rubbery soft-segment matrix. The structures of aliphatic and aromatic polyester exist simultaneously in BCL molecular chains. The properties of BCL copolyesters may vary from those of fragile plastic, to thermoplastic elastomer and then to hard plastic depending on the increase of hard segment content. One of the components-poly (ε-caprolacton) has remarkable compatibility with many polymers and is a good biodegradable polymer. So studies on BCL copolyesters may be of interest to further understand segmented copolymers and the miscibility of polymer blends.

BCL copolyesters were synthesized from monomers through a high-efficiency catalytic system. ε-Caprolactone(CL) monomer was vacuum distilled and 1,4-butanediol (BD) was first purified with molecular sieves for several days and then distilled under reduced pressure. Dimethyl terephthalate was an analytically pure product. The synthesis can be divided into two steps: First, DMT, BD and $Zn(OAc)_2$ were added into a nitrogen-purged reaction vessel and then heated to 170-220℃ to effect esterification and condensation. Second, CL monomer and $Sb(OAc)_3$ were added to bring about ring-opening polymerization (about 2hrs at 170-180℃) and then polycondensation under high degree of vacuum(<0.1mmHg) at 240-250℃. By changing the ratio of DMT to CL, we can synthesize a series of BCL copolyesters with different hard segment content.

The synthetic process of BCL copolyesters can be interpreted by the following equations:

$$CH_3OC\langle\rangle COCH_3 + HO(CH_2)_4OH \xrightarrow{Zn(OAc)_2} HO(CH_2)_4O\text{--}[C\langle\rangle CO(CH_2)_4O]_x H$$

$$C(CH_2)_5O + HO(CH_2)_4O\text{--}[C\langle\rangle CO(CH_2)_4O]_x H \xrightarrow[Vacuum]{Sb(OAc)_3}$$

$$HO(CH_2)_4O\text{--}[(C\langle\rangle CO(CH_2)_4O)_x(C(CH_2)_5O)_y]_n H$$

During the second process especially in the last step of condensation under high vacuum (<0.1mmHg), two types of transesterification between BT and CL segments occur since CL segment has difunctional group --COOH and --OH. It is the transesterification that makes the chain structures of BCL copolyesters more complicated than segmented polyurethane[1] and poly(ether-ester)[2].

The characterization parameters of BCL copolyesters are listed in **Table 1**. The chain structures of BCL copolyesters are investigated by high resolution ^{1}H-NMR spectroscopy. We can obtain the average compositions of hard and soft segments from the intensities of protons attached to benzene nucleus (8.08ppm) and protons attached to PCL carbonyl group--OCCH$_2$ (2.34ppm) respectively. The intensities of new peaks in the region of 4.0-5.0ppm which present the linkages between BT and CL segments are used to determine the BCL sequence structures[3,4]. From **Table 1**, it can be seen that both hard and soft segments are not very long especially for those with moderate hard segment content. Relatively the longer BT segment is hard to grow. This fact may be due to the conditions of synthesis that are more suitable for the growth of CL segments.

Table 1 The characterization parameters of BCL copolyesters*

	$[\eta]$ (dl/g)	Hard segment content(wt%)	L_S	L_H	Tg (K)	Tcc (K)	Tm (K)	Tc(K)
1	0.618	14	9.58	0.73	217		306	267
2	0.836	21	5.68	0.77	222	266	292	
3	0.638	27	4.20	0.80	227			
4	0.800	49	1.98	1.00	248	305	350	
5	0.682	69	1.72	1.96	264	289	409	350
6	0.706	78	0.69	2.53	294		473	437

*$[\eta]$--are measured in the solvent of 1,1,2,2-tetrachloroethene with U-viscometer at 30℃
L_S,L_H--the sequence length of soft and hard segment determined by ^{1}H-NMR
Tg--the glass transition temperature
Tcc--the temperature of cold crystallization in DSC heating runs
Tm--melting temperature in DSC heating runs
Tc--thermal crystallization temperature in DSC cooling thermograms

The solubility tests show that BCL copolyesters with hard segment content lower than 80% can be soluble in trichloromethane and all the samples are soluble in 1,1,2,2-tetrachloroethane. So the compositional homogeneity of BCL copolyesters are better than PBT-PTMG[5].

The DSC thermal analysis reveals that all the copolyesters exhibit only one glass transition temperature. The variation of Tg with copolymer composition is regular and can be described by Gordon-Taylor equation, as shown in the following. This suggests that BCL copolyesters have certain random copolymer property.

$$Tg = \frac{Tg_B + (KTg_A - Tg_B)W_A}{1 + (K-1)W_A}$$

Where W_A is the weight percentage of hard segment, $Tg_A = Tg_{PBT} = 315K$, $Tg_B = Tg_{PCL} = 213K$, $K = 0.48$.

The hard segments in our BCL copolyesters can crystallize and the correction of crystallinity is needed in the calculation. In our experiments, the glass transition temperature Tg was obtained by DSC heating thermograms after quenching. The cryatallinity of hard segments is so little that it has no influence on the change regular pattern of Tg with composition. As a result, the correction of crystallinity may be omitted.

The DSC thermograms of BCL copolyesters also exhibit only one not two melting endotherm associated with hard or soft segments in heating runs after quenching and only one thermal crystallization endotherm in slowly cooling from melt. So BCL copolyesters can either have hard segment crystallizing or soft ones but not both at the same time, which is very different from segmented polyurethane[6,7] and poly(ether-ester)[8,9]. The hard segments in BCL copolyesters with hard segment content higher than 50% can crystallize. The variation of melting temperature and enthalpy associated with BT or CL segment indicated that the crystallizability of BT or CL segments shows an increase with increasing each segment sequence length.

Table 2 The isothermal crystallization and temperature range for different spherulite morphology of BCL copolyesters*

Sample	Tc(K)	$T_{1/2}$(min)	Δ Hc (J/g)	Temp. for usual spherulite(K)	Temp. for unusual spherulite(K)
1	276	2.4	-29.5	298-303	
2	256	5.9	-18.6		
3					
4					323-343
5	372	4.6	-15.1	373-393	323-383
6	443	1.4	-13.5	453-463	323-443

*Tc, Δ Hc --the temperature and enthalpy of iso-crystallization
$t_{1/2}$--the time at which the crystallization degree reaches half

The isothermal crystallization behavior and spherulite morphology of BCL copolyesters are investigated by DSC and PLM. The results are listed in **Table 2**. It is shown that for BCL copolyesters with low and high hard segment content, CL segment or BT segment is long enough to crystallize and grow spherulites under appropriate conditions. The BT hard segments in copolyesters can grow usual spherulites at higher temperature and unusual spherulites at lower temperature. An interesting finding is that the crystallization of soft segment requires considerably long sequence length (about 5-6 units), while that of hard segment requires much shorter sequence length only one BT unit. Further researches and performances tests are in progress.

Acknowledgment

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