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BIODEGRADABLE LIQUID CRYSTALLINE POLYESTERS OF HYDROXYPHENYLALKANOIC ACIDS: SYNTHESIS AND IN VITRO DEGRADATION STUDIES OF POLY[3-(4-OXYPHENYL)-PROPIONATE-CO-4-OXYBENZOATE]

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BIODEGRADABLE LIQUID CRYSTALLINE POLYESTERS OF HYDROXYPHENYLALKANOIC ACIDS: SYNTHESIS AND IN VITRO DEGRADATION STUDIES OF POLY[3-(4-OXYPHENYL)-PROPIONATE-CO-4-OXYBENZOATE]

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ABSTRACT

Liquid crystalline copolyester of 3-(4-hydroxyphenyl)propionic acid (HPPA) of natural origin with 4-hydroxybenzoic acid (HBA) was synthesized by direct acidolytic polycondensation of the pure acetoxy derivatives of the monomers. The copolyesters were characterized by IR and NMR spectroscopy and by viscosity, TGA, DSC and PLM measurement. The HPPA/HBA50:50 copolyester showed birefringence with nematic schlieren texture above 220°C with melt processability. The *in vitro* hydrolytic degradability of the polyesters was studied by noting water absorption in buffer solutions of pH 7 and 10 at 30 and 60°C. The degradation observed at 30°C and pH 7 was 0.7 wt%, in the case of HPPA/HBA50:50 copolyester after 340 hours. At pH 10 and at 60°C, the degradation reached 2.75 wt% after 340 hours. The degradation was also proven by DSC, TGA, WAXD, and SEM techniques. The results indicated considerable degradation compared to commercial Vectra®.

Key Words: 3-(4-Hydroxyphenyl)propionicacid; Biodegradable liquid crystalline polyesters; Poly(oxyphenylalkanoates).

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INTRODUCTION

Aromatic liquid crystalline polymers are well known for their high mechanical properties with improved processability due to the spontaneous orientation in their melt [1]. However, fully aromatic commercial polyesters are, not biodegradable and hence, cannot be used in biodegradable/biomedical devices where strength with biodegradability is a requirement [2] Recently, there have been a few attempts at developing biodegradable liquid crystalline polymers [3-5]. Copolymerization of aliphatic hydroxy carboxylic acids with aromatic hydroxy carboxylic acids was adopted as a strategy [5]. Due to poor copolycondensation and low thermal stability of aliphatic hydroxy carboxylic acids, this strategy is not satisfactory. It was also reported that polyesters with ester carbonyl attached to aliphatic segments are prone to enzymatic degradation compared to that attached to aromatic or unsaturated groups [6]. Use of aromatic monomers having aliphatic methylene segments attached directly to the aromatic moiety, such as phenolic derivatives of alkanoic acids is considered a another important strategy [6, 7]. The aliphatic carbonyl group is expected to introduce hydrolytic degradability [8]. Thus, copolyesters of hydroxy phenyl alkanoic aicds such as 3-(4-hydroxyphenyl)acetic aicd (HPAA) and 3-(4-hydroxyphenyl)propionic acid (HPPA) with HBA which are non-toxic and occur in the metabolism of plant or animal are expected to give biodegradable LC polyesters [3].

As part of a serious study on the polyesters derived from hydroxyphenylalkanoic acids [9-11], we have reported the polymerization, characterization and *in vitro* degradation of the homopolyester of HPAA and its copolymerization with HBA [10]. Considering the potential of these copolyesters for various applications particularly in the biomedical area, it is apparent that a detailed study on the homopolymerization of HPPA and its copolymerization is also required. It was Elias and Warner who first prepared a brown colored copolymer of HPPA with HBA through an interfacial polycondensation method [12]. Imasaka *et al.* [13] showed that the copolyesters of HPAA or HPPA with lactic acid were biodegradable. In an attempt to prepare biodegradable liquid crystalline polymers, Rajalekshmi and Pillai observed a smectic phase in the case of the copolyester of HPPA/HPAA with 8-(3-hydroxyphenyl)octanoic acid [9]. Kricheldorf and Conradi showed that copolymerization of HPPA with HBA gives rise to biodegradable thermotropic copolyesters [14]. They employed a one-pot method using acetic anhydride for the synthesis of LC copolyester of HPPA with HBA, as the preparation of the acetoxyderivative of HPPA in pure form met with difficulties [14]. Later, Kricheldorf and Stukenbrock adopted another technique involving silylprotected acetoxy derivative of HPPA to prepare LC copolyesters of HPPA with hydroxy acids such as HBA, vanillic acid and gallic acid [3]. They also used this method to prepare LC hyperbranched or star-shaped copolyesters of HPPA with HBA [15, 16]. They could only obtain polyesters with inherent viscosity of 0.5-0.7 dl/g which is still in the borderline requiring further improvements. The silyl method of Kricheldorf and his group [3] requires higher reaction temperatures and presence of catalysts to obtain high molecular weight and homogeneity of the copolyester. It appears, therefore, that a reinvestigation/improvement in the method of preparation of the HPPA/HBA copolyester synthesis would be interesting. Commercially, acidolytic polycondensation using the pure acetoxy derivative of the monomer is considered to be cost effective [2, 17]. This method is also expected to give rise to high molecular weight random copolyesters at a lower polymerization temperature in the absence of transesterification catalysts. In the present work, LC copolyester of HPPA with HBA is synthesized by acidolytic polycondensation in the melt using a pure acetoxy derivative in the presence of a trans-esterification catalyst. The LC copolyesters were characterized for their thermal, phase behavior and *in vitro* hydrolytic degradability. Post polymerization has also been adopted to improve the properties of the polymer [18].

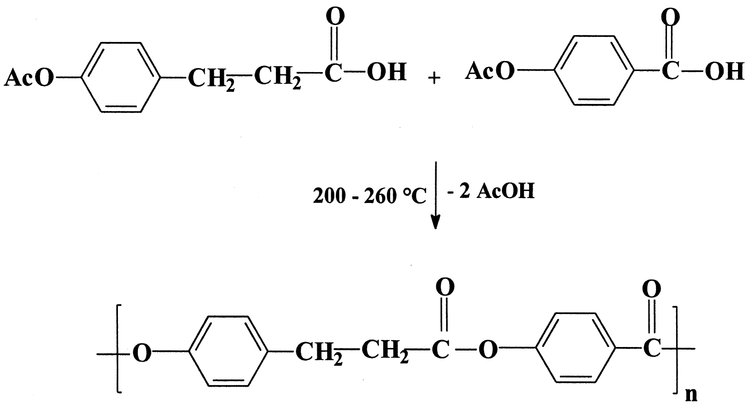
EXPERIMENTAL

Materials

4-Hydroxyphenylacetic acid, 3-(4-hydroxyphenyl)propionic acid (phloretic acid), 4-hydroxybenzoic acid and magnesium acetate tetrahydrate (99% purity) were purchased from Aldrich Co., (Milwaukee, WI), and were used without further purification. Acetic anhydride (AR), anhydrous sodium acetate (AR), glycine, dichloromethane (DCM), and sodium hydroxide were purchased from S. D. Fine Chemicals, India and Dowtherm® (a mixture of isomeric di- and tri- benzylbenzenes) and trifluoroacetic acid (TFA) were purchased from Spectrochem (Mumbai, India). Acetic anhydride and Dowtherm® were purified by distillation. All the solvents and other reagents used were of AR grade and used after distillation. 4-Acetoxy benzoic acid (ABA) was prepared by the acetylation of HBA using acetic anhydride [19].Vectra® A900 was received as a gift from Hoechst Celanese, USA.

Methods

3-(4-Acetoxyphenyl)propionic acid (APPA) was prepared by heating 16.6 g (0.10 mol) of HPPA and 20 g (0.20 mol) of acetic anhydride in the presence of sodium acetate anhydrous, as catalyst (0.20 wt%) for 2 hours at 80°C and cooled and poured into 50 g crushed ice and allowed to settle. It was then filtered and air-dried. Finally, APPA was recrystallized from acetone and dried under vacuum at 60°C for 2 hours. Colorless crystals of APPA were obtained. Yield 75%, m.p. 95°C. Elemental Analysis Calcd. for $C_{11}H_{12}O_4$, C, 63.45, H, 5.81; Found: C, 63.27, H, 5.51; ^{1}H NMR ($CDCl_{3/}TMS$), δ (ppm): 2.2 (s, 3H, CH_3), 2.65-2.7 (t, 2H, CH_2), 2.86-2.93 (t, 2H, CH_2), 6.9-7.26 (4H, Ar). HPLC was carried out using Shimadzu HPLC silica column with 100 methanol as eluent. 99.93% eluted at 1.8 minutes as single peak (MW=207).



Scheme 1. Synthesis of HPPA/HBA copolyesters.

Preparation of Copolyesters

All the copolyesters of HPPA and HBA were synthesized by the acidolytic transesterification method in the melt (Scheme 1). A glass reactor was employed for the synthesis [19].

Melt Polycondensation

In the acidolytic melt polycondensation, acetoxy derivatives of the hydroxy acids were condensed in the melt at 220-240°C for 4-6 hours. Vacuum was applied at the final stage of polycondensation for 0.5-1 hours. In a typical procedure, APPA, 1.94 g (10 mmol) ABA, 1.64 (10 mmol) magnesium acetate tetrahydrate (1 mg) were weighed into the cylindrical glass reactor equipped with magnetic stirrer, gas-inlet, and gas-outlet tubes. The reaction vessel was flushed with nitrogen and immersed up to the neck into a salt bath preheated to 200°C. The reaction was carried out under inert atmosphere for 1 hour at 220°C. The temperature was increased to 240°C and acidolytic condensation continued under this condition for 4 hours, and reaction was continued under vacuum (0.01 mm of Hg) for 1 hour. After completion of polymerization, the temperature of the bath was slowly reduced to 180°C and the product was chipped out of the reactor, powdered, and purified by Soxhlet extraction using acetone-isopropanol mixture (60:40 by volume) for 16 hours and dried at 80°C in vacuum or by precipitation in excess of cold methanol from a solution of the polymer in a DCM/TFA mixture (4:1 by volume), filtered and dried under reduced pressure at 60°C.

HPPA:HBA 50:50. Elemental analysis (%): Calcd.: C, 71.61; H, 4.47, Found: C, 71.40; H, 4.28.

FTIR (KBr pellet, cm^{-1}): 3494 (ν_{OH} Ar, b), 3036 ($\nu_{C\text{-}H}$, Ar), 2928, 2861 ($\nu_{CH2,}$ Ali.), 1755 ($\nu_{C=O}$ s), 1607 ($\nu_{C=C}$ Ar, s). ^{1}H NMR ($CDCl_3$/TFA 4:1): $\delta = 2.2$ (s, 3H,

CH_3), 4.0 (m, 4H, CH_2), 7.0-7.5, (m, 4H, Ar-H) 8.2-8.3 (m, 4H, Ar-H) ppm. ^{13}C-NMR ($CDCl_3$/TFA 4:1): δ 174.5, 173.2, 167.5, 166.7 (O=C-OH), 150 (Ar C-O), 132.6 (Ar), 131.2 (Ar), 131.0 (Ar), 122.5 (Ar), 122.2 (Ar), 40.9, 36.0 (-CH_2-), 20 (-CH_3) ppm.

Post Polymerization

All the copolyesters were post polymerized under inert atmosphere at 220-240°C for 8-16 hours and purified by solvent extraction as described above.

Degradation Studies

In order to investigate the *in vitro* degradation of the polyesters, button shaped samples of the polyesters were compression molded by melt-pressing technique in 10 mm diameter and 2 mm thickness, by heating the powdered sample in a cylindrical MS mold at 120-200°C under a pressure of 200 kg cm^{-2} using a Spectralab hydraulic press of the film making unit.

The buffer solution of pH 10 was prepared by mixing 25 ml of a 0.2 M solution of glycine with 16 ml of a 0.2 M sodium hydroxide solution in distilled water and diluting it to 100 ml [19]. A buffer solution of pH 7 was prepared by dissolving the buffer tablet of pH 7 in 100 ml of distilled water.

Measurements

The inherent viscosity, (η_{inh} was measured using a Ubbelohde viscometer thermostated at 30 ± 0.1°C. The polymer solution (2g/L) in DCM /TFA(4:1 by volume) as solvent was used in all cases.

The IR spectra were recorded with a Nicolet magna 560 FTIR spectrometer. The ^1H and ^{13}C NMR spectra were recorded with a Bruker 300 MHz FTNMR spectrometer using TFA/$CDCl_3$ (1:4 by volume) as a solvent. Tetramethylsilane (TMS) was used for internal shift referencing in all cases. 5 mm o.d. sample tubes were used for the ^1H and 10 mm o.d. sample tubes for the ^{13}C NMR spectra.

The differential scanning calorimetry (DSC) measurements were conducted with TA instruments DSC 2010 connected with thermal analyst 2100 system, in non-hermetic crimped aluminium pans under nitrogen purge of 50 ml/min. Thermogravimetric analysis (TGA) was conducted with a Du Pont TGA 951 connected with a thermal analyst 2000 system under air, as well as nitrogen at a flow rate of 50 ml/min.

The wide-angle X-ray diffraction (WAXD) powder patterns were recorded on a Rigaku D_{max} powder diffractometer using Ni-filtered CuK_α radiation from 2θ = 0- 45°. Phase behavior was studied using a Nikon Optiphot polarized light optical microscope attached with a Linkam 600 heating and freezing stage.

The water content of the polymer was determined by soaking the film samples in a buffer solution of pH 10 or pH 7 at 30 or 60°C. At every fixed period of time, the specimens were taken out for weighing. Samples were gently blotted prior to the weighing to remove the excess surface water. The water content is expressed as percentage of the initial dry polymer. Reported water contents were the average of 5-10 specimen determinations. The degree of the in vitro degradation and water absorption of the polymer were evaluated according to Equations 1 and 2, respectively [5].

$$\text{Degree of } \textit{in vitro} \text{ degradation (\%)} = 100\,(W_0 - W_D)/W_0 \tag{1}$$

$$\text{Water absorption (\%)} = 100\,(W_W - W_D)/W_W \tag{2}$$

where W_0 is the initial weight of the polyester sample, W_W is the wet weight of the copolymer after hydrolyzing for a desired period in the buffer solution and W_D is the weight of the dried copolymer sample after hydrolyzing for a desired period in a buffer solution.

FTIR absorption of the degraded film was measured using dried virgin films taken out periodically. Scanning Electron Microscope (Hitachi 2403 A, Japan) was used for the surface morphology studies of the degraded samples.

RESULTS AND DISCUSSION

Synthesis of Copolyesters

HPPA/HBA copolyesters were prepared by acidolytic melt polycondensation by varying the compositions of HPPA and HBP. All the copolyesters were obtained in good yield and were completely soluble in TFA/DCM unlike the products of one-pot and silyl methods described earlier (Table 1) [3, 14]. Kricheldorf *et al.*· [3] and Lieser *et al.* [20], however, showed that random copolyesters exhibited better solubility characteristics**.** The complete solubility of the HPPA/HBP 50:50 copolyesters obtained by acidolytic melt polycondensation indicates extensive randomization. Moreover, ^{13}C NMR spectra of the copolyester displayed four CO signals of nearly equal intensity. The four CO signals of nearly equal intensity observed between δ 164-174 ppm represent the four posssible diads and thus, proved the existence of a random sequence [3]. The solubility of the copolyesters decreased with increase in HBA content as also observed by previously [14]. Copolyesters with higher HBA contents (above 60 mol%) showed evidence of blocks of HBA units. The FTIR spectra of the copolyesters showed the characteristic bands typical for the homopolyesters.

Extensive experiments carried out in the presence and absence of the transesterification catalyst showed the catalyst does not have any effect on the overall properties of the polymer except that it reduces the time of polymerization substantially. It was also noted that the reaction can be carried out at a lower tempera-

Table 1. Data on Synthesis of HPPA/HBA Copolyesters

Exp. No.	Polycondensation Method[a]	Temp.[a,b] °C	Time[a,b] h	Yield %	η_{inh}[c] dL/g	Solubility[d]
1	Melt polycond.: HPPA/HBA50:50a	200, 240 260V	0.5, 8.0, 2.0V	84	1.1	ins. THF, sol. DCM/ TFA
2	Melt polycond. with $MgAc_2$: HPPA/HBA50:50b	200, 240 240V	0.5, 3.0, 1.0V	85	1.1	ins. THF, sol. DCM/ TFA
3	Melt polycond. with $MgAc_2$ and PC HPPA/HBA50:50	200, 240 240V, 220	0.5, 3.0, 1.0V, 8.0	85	1.2	ins. THF, sol. DCM/ TFA
4	Melt polycond. with $MgAc_2$ and PC HPPA/HBA40:60	200, 240 240V, 220	0.5, 3.0, 1.0V,10.0	75	—	ins. THF, spar. sol. DCM/ TFA
5	Melt polycond. with $MgAc_2$ and PC HPPA/HBA60:40	200, 240 240V, 220	0.5, 3.0, 1.0V, 6.0	84	1.2	ins. THF, sol. DCM/ TFA

[a] PC = post condensation

[b] V= vacuum was applied

[c] measured at 30 °C with c = 2g/L in DCM/TFA (volume ratio 4:1)

[d] THF= tetrahydrofuran, DCM = dichloromethane, TFA = trifluoroacetic acid

ture (due to the presence of the acidic proton) without causing side reactions unlike in silyl protected carboxyl group. In the present experiments, formation of the homogeneous random copolymers was noted even in the absence of an additional catalyst, due to the catalytic effect of the acidic protons, whereas in the case of silylated monomer soluble and random copolymers were only obtained in the presence of titanium isopropoxide or similar catalysts [3].

Thermal and Phase Properties of Copolyesters

In the case of HPPA/HBA copolyesters, the results obtained by DSC, PLM, and TGA analysis are summarized in Table 2. The DSC traces of the copolyesters show, in addition to the Tg, a reversible first order transition corresponding to mesophase formation (Figure 1). With increasing the content of HBA, the transition enthalpy decreases and at a comonomer ratio of 50:50 this transition has minimized or spread over a long range, but did not completely vanish. DSC traces of the HPPA/HBA50:50 copolyester showed two endotherms with peak maxima corresponding to 230°C and 320°C, and on cooling, one exotherm was observed at 180°C. Under PLM, a homogeneous birefringent melt was observed above 220°C, with clear schlieren texture typical for a nematic phase (Figure 2). Annealing indicated narrowing of the LC transition. In the case of HPPA/HBA copolyesters, when the molar fraction of HBA increased above 50%, the stability of the LC phase increases to such an extent that an anisotropic-isotropic transition is not

Table 2. Properties of HPPA/HBA Copolyesters

HPPA/HBA	Tg	Tm	Ti	Tnc[a]	Phase transitions[b]	T_5	T_{10}	T_{50}[c]
Copolyester	(°C)				(°C)	(°C)		
HPPA/HBA50:50a	50	220	310	188	C 200 N 350 I	439	454	504
HPPA/HBA50:50	50	230	320	190	C 230 N 400 I	447	459	509
HPPA/HBA60:40	-	230	315	188	C 230 N 310 I	334	359	424

[a] determined by DSC measurements with a heating rate of 10 °C /min , Tnc = nematic - crystalline transition

[b] optical microscopy with crossed polarizers, C - crystal and I - isotropic

[c] determined by TGA measurements with a heating rate of 20 °C /min under nitrogen purge, T_5 = temp. at 5% decomposition

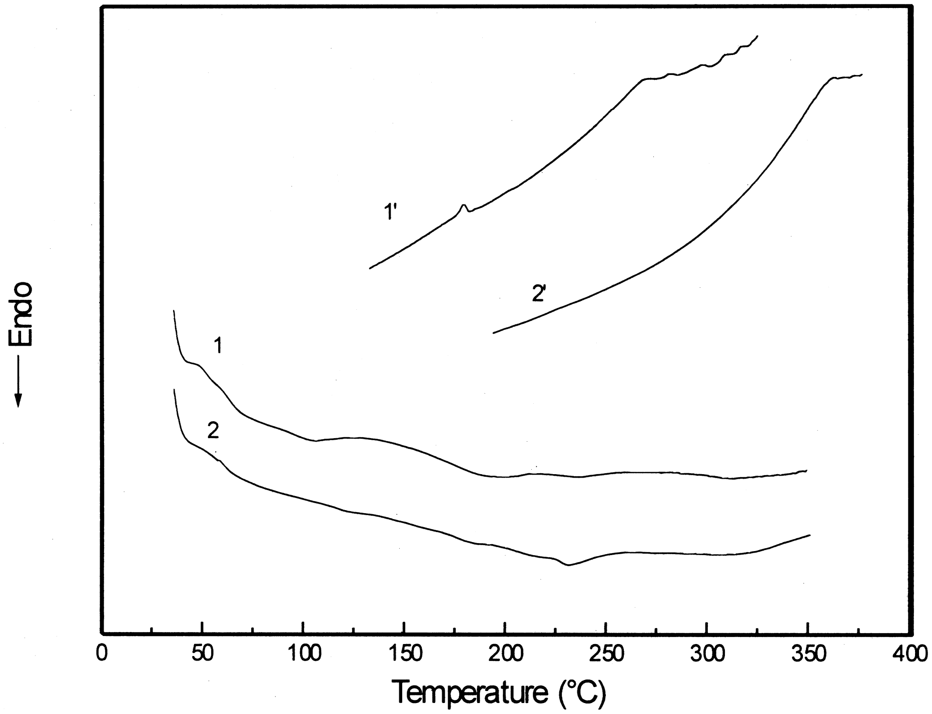


Figure 1. DSC curves (heating and cooling rate 20°C/min) of HPPA/HBA copolyesters.

clearly detectable. A further increase in the HBA content > 60 mol% results in a third type of DSC traces that exhibit an endotherm at about 325°C and an exotherm upon cooling at about 280°C. This fits exactly in with a solid-solid transition of polyHBA [21]. TGA of the copolyesters showed a thermal stability above 400°C, which on annealing showed further increase with time. As the time of annealing at temperatures between Tg and Tm increases, the thermal stability of the polymer becomes higher. This may be explained by enhanced crystallinities

Figure 2. Schlieren texture of HPPA/HBA 50:50 copolyester at 250°C.

and higher perfection of crystallites. Field *et al.* [22] reported an increase in thermal stability of the copolyesters with annealing.

LC films of the copolyester were made on a film-making unit. HPPA/HBA50:50 copolyester showed better processability when films were melted. Under a pressure of 100 kg/m^2, the entire material was found to exhibit plasticity at 70-100°C above Tg. Under slight pressure at 140-160°C, or without pressure at 200-220°C, formation of a mobile melt was observed.

WAXD Studies of the Copolyesters

In the case of HPPA/HBA50:50 copolyeste,r a broad peak was observed at 2θ corresponding to 20° which indicated the lateral ordering of polymer chains with d spacing 4.37 A. An additional broad peak was observed at lower angles unlike in homopolyesters between 3-5° indicating decreased ordering along the rigid segments. These two typical transitions agree with the existence of a frozen nematic phase with a high degree of hexagonal chain packing.

Water Absorption and Hydrolysis Degradation of Copolyesters

The *in vitro* degradation studies of the copolyesters of HPPA/HBA5050 were carried out in buffer solutions of pH 7 and pH 10 at 30 and 60°C. A wholly aromatic commercially available LC polyester, Vectra® was used as a control in all the experiments since it is known to be highly resistant to hydrolysis under these conditions [2]. Enzymatic degradation studies could not be carried out as there are no known enzymes that grow on LC polyesters [3].

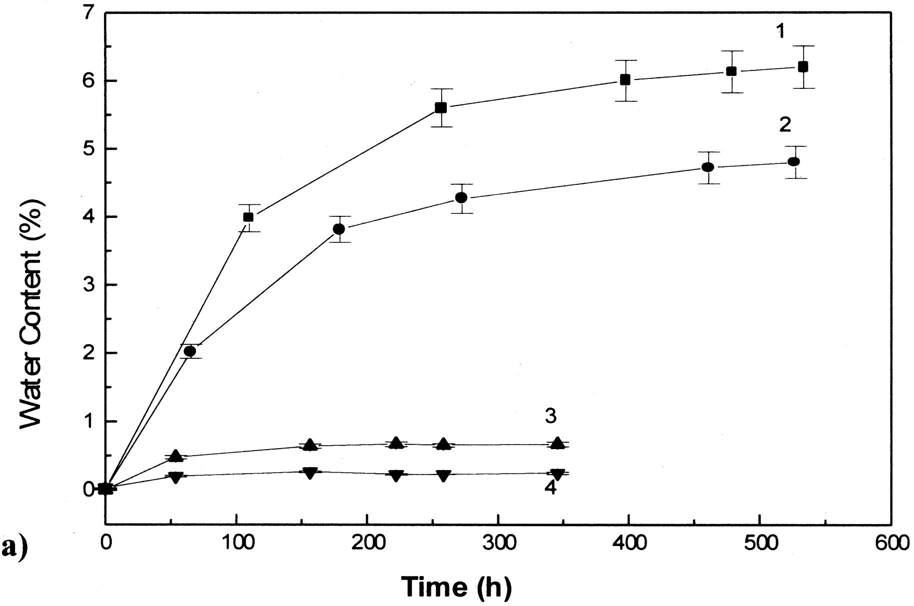
Water absorption (wt%) and degradation (wt%) vs. time in buffer solutions of pH 7 and pH 10 at 30.0 and 60.0°C, observed in the case of copolyesters of HPPA are shown in Figures 3 and 4. In the case of HPPA/HBA copolyester, water absorption of 3.8 and 5.5% was observed at 30 and 60°C, respectively in the buffer solution of pH 7. At pH 10, the corresponding water content (wt%) observed after 340 hours of degradation was 4.5 and 6.1 at 30 and 60°C, respectively. At room temperature and neutral pH, the degradation observed in the case of HPPA/HBA50:50 copolyester was 0.70 wt% after 340 hours, whereas when the temperature was raised to 60°C, a degradation increase was observed up to 0.9 wt%. At higher pH, the degradation showed an increase up to 2.75 wt% at 60°C after 340 hours.

The observed decrease in degradation of HPPA/HBA copolymers compared to that of HPAA/HBA copolyesters can be attributed to the increased packing and LC orientation which reduces the penetration of water [11]. In addition to that, the decreased electrophilic character of ester carbonyl in HPPA might also have been a contributor. Similar results have been reported by Imasaka *et al.* [13] who observed that HPAA containing copolyester showed an increased degradation compared to HPPA containing copolyesters with lactic acid. The higher the degradation rate observed in the case of the HPPA/HBA50:50 copolymers with increasing pH and temperature of the buffer solution may be attributed to a similar situation as explained in the case of HPAA/HBA copolyesters [11]. It is also known that the degree of crystallinity of polymers is an important factor in polymer degradation since crystalline regions degrades slower than amorphous ones. The amorphous phase contains more free volume which eases the invasion of water.

Unlike those nondegradable polyesters such as Vectra®, which usually attained its water absorption equilibrium with a water content of $< 0.5\%$ in two weeks' time, water absorption equilibrium was never attained for the copolyesters during this period. Jin *et al.* [5] reported similar observations in the case of *in vitro* hydrolytic degradation of biodegradable thermotropic ternarypolyesters of HBA, glycolic acid and 4-hydroxycinnamic acid.

Imasaka *et al.* [23] showed that a significant change in degradation kinetics was observed with a change in pH and temperature in the case of terpolyesters of lactic acid, mandelic acid and HPPA, since polyesters are usually base sensitive. Leong *et al.* [24] noticed an increase in degradation with increasing pH in the case of polyanhydrides. Furthermore, it is also evident that increasing the molecular weight could lower its hydrolysis ability. In addition to the water absorption behavior of the polyester, there is the possibility of change in its actual molecular weight. This can be followed by a measurement of the inherent viscosity value. A decrease in inherent viscosity value with degradation time from 1.2 dl/g to 0.4 dl/g was observed for HPPA/HBA50:50 at 60°C after 340 hours of degradation in

(a)



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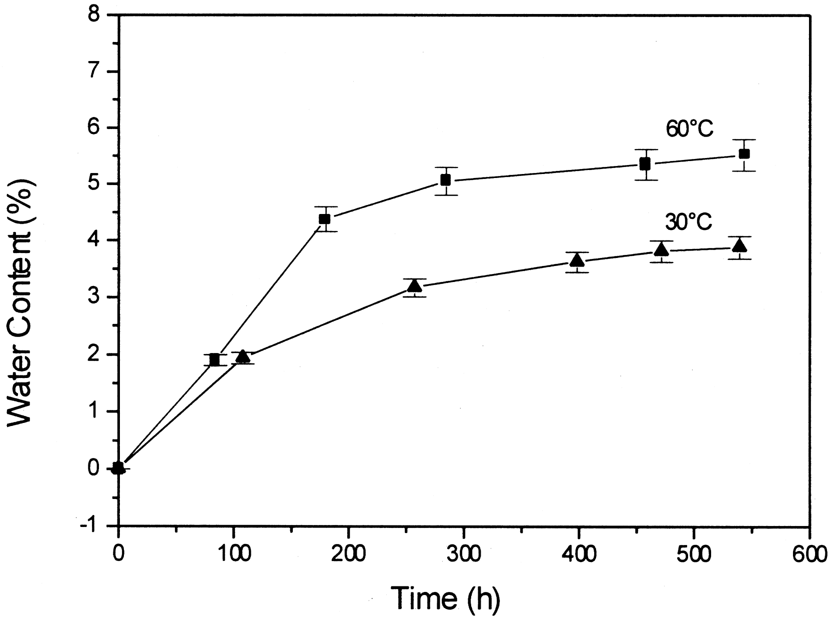

Figure 3. Water absorption vs degradation time for HPPA/HBA50:50 copolyester at 30°C and 60°C; (a) pH 10, (1) HPPA/HBA50:50 at 60°C, (2) HPPA/HBA50:50 at 30°C, (3) Vectra at 60°C, (4) Vectra 30°C; (b) pH 7, HPPA/HBA50:50.

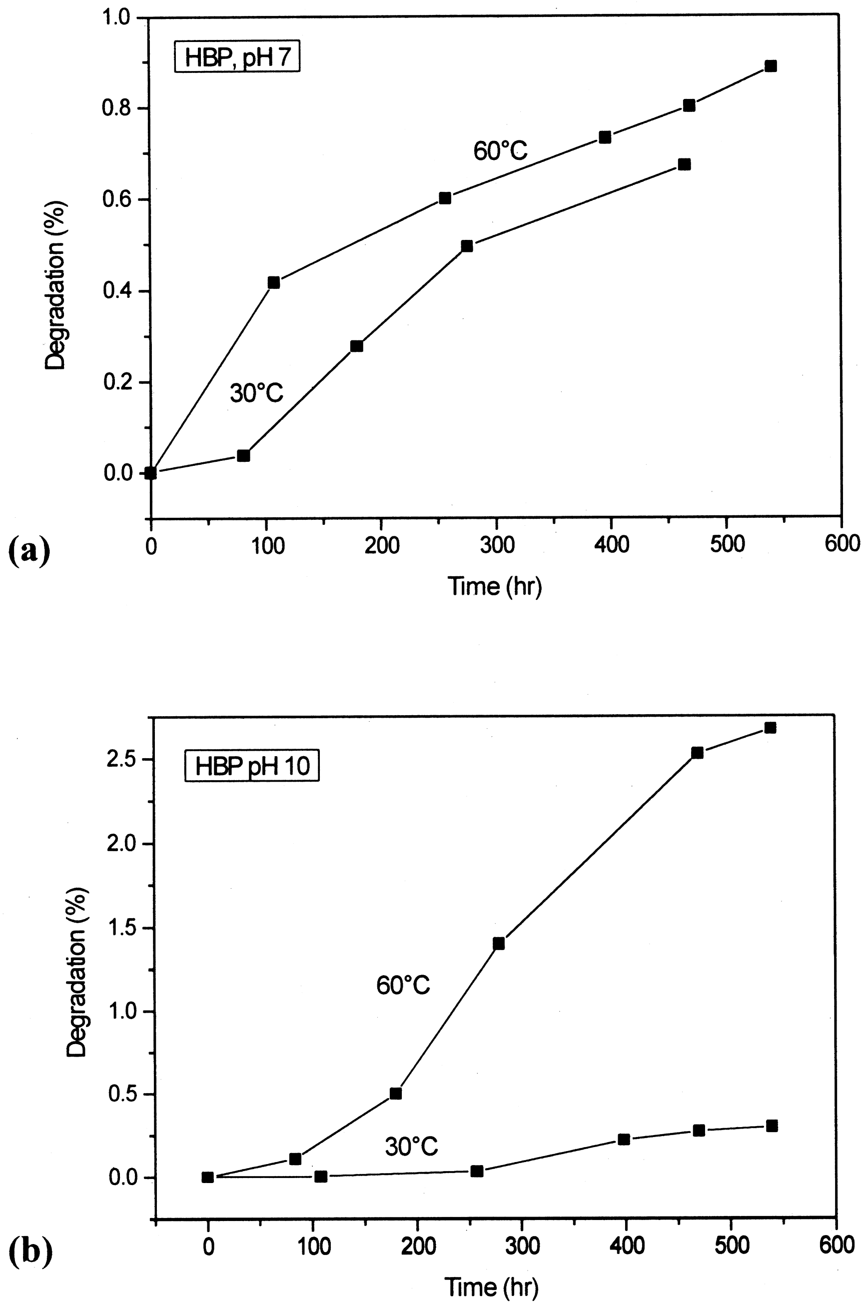

Figure 4. % Degradation vs. time for HPPA/HBA50:50 copolyester in buffer solutions of at 60°C and 30°C: (a) pH 7; (b) pH 10.

a buffer solution of pH 10. Jin *et al.* [5] also reported a similar reduction in inherent viscosity in the case of LC terpolyesters of HCA/HBA/GA.

Characterization of the Degraded Polymer

Generally, the degradation of polymer is a result of the depression of the molecular weight and is characterized by the property loss [5]. In homo and copolyesters, the FTIR and TGA measurements give further evidence that chemical degradation occurred during the water absorption process and that the degradation resulted from hydrolysis of the ester bonds in the copolyester. The changes in the FTIR absorbance ratio, $A_{1730/}A_{1613}$, for the copolyesters gave a direct evidence for the scission of the copolymer during hydrolysis (2.0 to 1.54 after 280 hours). The decrease in the characteristic absorbance of HPPA carbonyl bands with increasing hydrolysis time indicate ester bond breaking. It should also be mentioned that the presence of degradable HPPA segments could induce the degradation of the aromatic by acid catalysis as indicated by lowering of the ratio of the carbonyl absorption, A_{1735} with aromatic C-C stretching frequency, at $A_{1600.}$

Degradation of the polymer not only alters the chain structure as discussed above, it should also lead to a reduction of physical and mechanical properties. DSC measurements were performed to clarify the relationship between the changes in sequence distribution and packing structure of the polyester. The DSC curves of HPPA/HBA50:50 subject to treatment in a buffer solution of pH 10 at 60°C, are shown in Figure 5. It was observed that the melting transition shifted

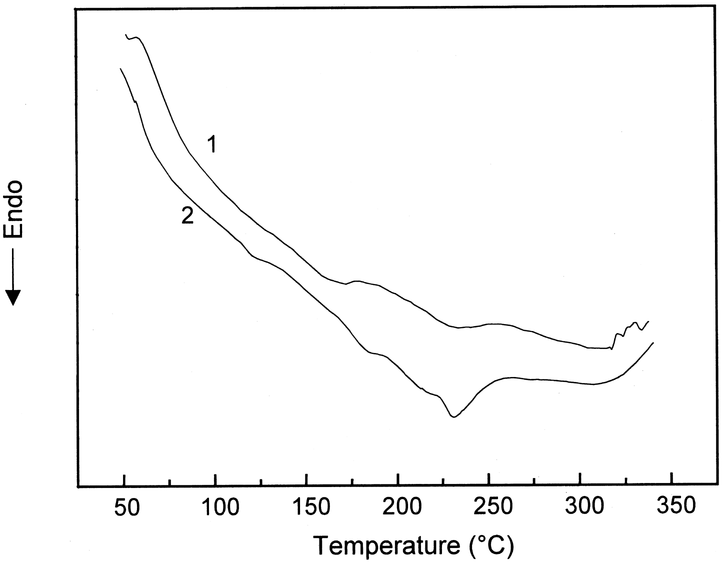

Figure 5. DSC traces of original and degraded HPPA/HBA50:50 copolyester film: (1) degraded in pH10/60°/480 hours; (2) original film.

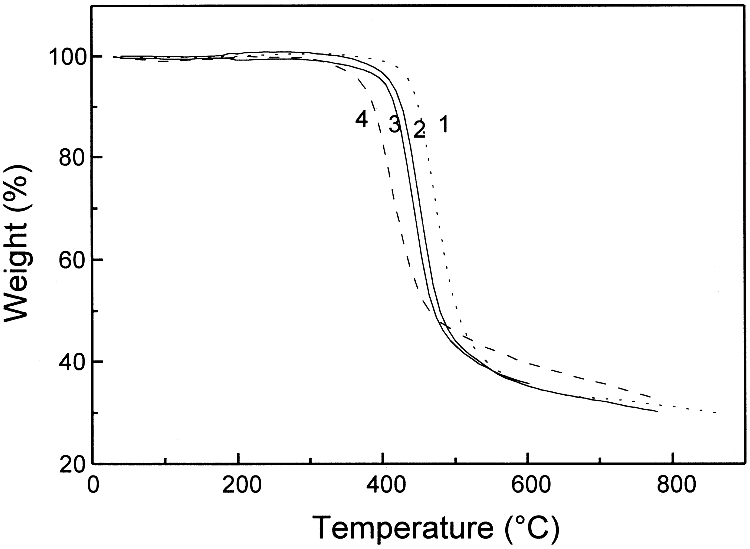

Figure 6. Dynamic TGA traces (at 20°C/min) of original and degraded HPPA/HBA50:50 copolyester films at 60°C: (1) original film; (2) pH 7, 180 hours; (3) pH 7, 280 hours; (3) pH 10, 540 hours.

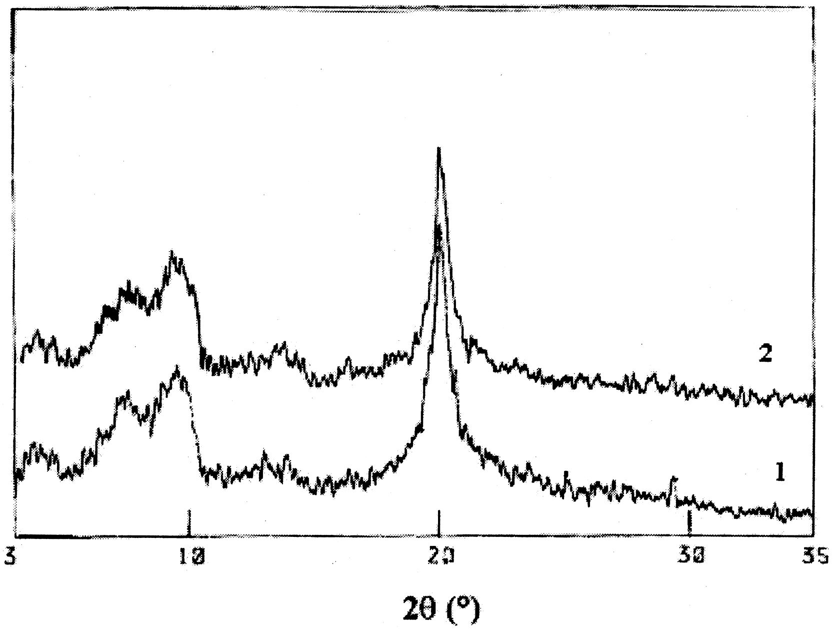

Figure 7. WAXD powder patterns of HPPA/HBA50:50 films after degradation in a buffer solution of pH 7 at 60°C for 540 hours: (a) original film; (b) degraded for 190 hours in pH 7/60°C.

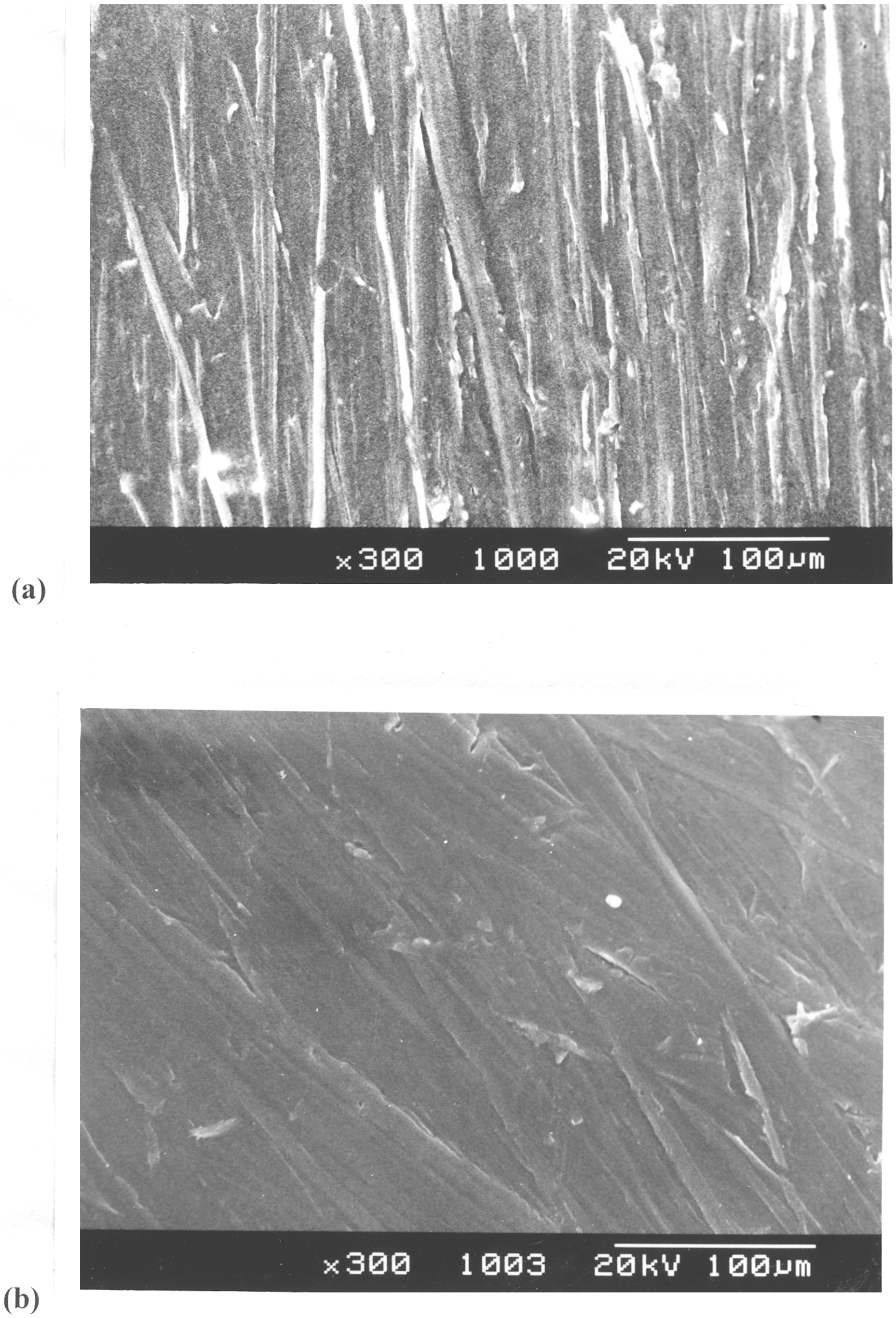

Figure 8. SEM micrographs of original and degraded HPPA/HBA50:50 films: (a) Surface of degraded film in pH, 10/60°C/420 hours; (b) Surface of original film.

towards lower temperature, the peak width became narrower with the corresponding area was almost unchanged indicating a crystal with a more perfect packing and a smaller size in the degraded copolymer. Jin *et al.* [5] reported a similar observation in the case of DSC of degraded LC terpolyesters of HCA, GA and HBA. This fact means that the molecular weight of the copolymer decreases by scission of the main chain and also that the hydrolysis by water occurs preferentially in the amorphous regions of the copolymer.

The dynamic thermogravimetric analysis of the copolymer clearly shows that the longer the degradation time, the lower the thermal stability due to the formation of the lower molecular weight species after hydrolytic degradation in the case of copolyesters (Figure 6).

The WAXD analysis on the degraded HPPA/HBA50:50 samples suggested that the hydrolytic degradation could lead to a slight reduction of its amorphous fraction because an apparent enhancement of the degree of crystallinity is observed with the increase of the hydrolysis time in the case of the copolyesters (Figure 7).

The SEM of the degraded HPPA/HBA50:50 copolymer film surface in comparison to the control samples were given in Figure 8. It is visible that some surface erosion has taken place on the surface of the film. Kricheldorf *et al.* [24] observed similar surface erosion in the case of degraded aromatic polyesteranhydrides. A similar degradation by surface erosion was also reported by Vert *et al.* [25]. Hence, the SEM micrographs support the hypothesis of degradation by surface erosion.

CONCLUSION

The present study shows that high molecular weight, random copolyesters of HPPA with HBA can by synthesized by acidolytic melt condensation of the pure acetoxy derivative of the monomers. HPPA/HBA50:50 copolyester showed melt processability with clear schlieren nematic texture above 220°C and thermal stability around 400°C.

HPPA/HBA50:50 showed in vitro hydrolytic degradability in buffer solution of pH 7 at 30°C. The *in vitro* degradation studies indicated that the degradation of these polyesters is probably governed by parameters such as crystallinity, mesophase character and nature of the polyester. These findings are significant because of the possible applications of these polymers as biodegradable LC polyesters in biomedical implants such as artificial screws, pins and in biomedical composites.

REFERENCES

1. Han, H.; Bhowmik, P. K. Prog. Polym. Sci. **1997**, *22*, 1431.
2. a. Ober, C. K.; Jin, J. I.; Lenz, R.W. Adv. Polym. Sci. **1984**, *13*,103.

b. Jin, J. I.; Kang, C-S. Prog. Polym. Sci. **1997**, *22*, 937.

3. Kricheldorf, H. R.; Stukenbrock, T. Macromol. Chem. Phys. **1997**, *198*, 3753.
4. Jin, X.; Carafagna, C.; Nicolais, L.; Lanzetta, R. J. Polym. Sci., Polym. Chem. Ed. **1994**, *32*, 3115.
5. Jin, X.; Carafagna, C.; Nicolais, L.; Lanzetta, R. Macromolecules **1995**, *28*, 4785.
6. Elke, R.; Ilona,. K.; Uwe, W.; Mueller, R.-J.; Deckwer, W.-D. Macromol. Symp. **1998**, 130.
7. Kricheldorf, H.R.; Wahlen, L.; Stukenbrock, T. Macromol. Symp. **1998**, *130*, 261.
8. Hammet, L. P. *Physical Organic Chemistry Reaction Rates, Equilibria and Mechanisms*, McGraw-Hill: Kogakusha, Tokyo, 1970, p. 352.
9. Rajalekshmy, S.; Pillai, C. K. S. In, *Macromolecules Current Trends*, Vol. 2, Venkatachalam, S.; Joseph, V.C.; Ramaswamy, R.; Krishnamurthy, V.N., Eds. Allied Publishers: New Delhi, India, 1995, p. 591.
10. Prasad, V. S.; Pillai C. K. S.; Kricheldorf, H. R. J. Polym. Sci., Polym. Chem. **2001**, in press.
11. Prasad, V. S.; Pillai, C. K. S. J. Polym. Sci., Polym. Chem. **200**1, in press.
12. Elias, H.G.; Warner, R. J. Makromol. Chem. **1981**, *182*, 681.
13. Imasaka, K.; Nagai, T.; Yoshida, M.; Fukuzaki, H.; Asano, M.; Kumakura, M. Makromol. Chem. **1990**, *191*, 2077.
14. Kricheldorf, H. R.; Conradi, A. J. Polym. Sci., Polym. Chem. **1987**, *25*, 489.
15. Kricheldorf, H. R.; Stukenbrock, T.; Friedrich, C. J. Polym. Sci., Polym. Chem**.** **1998**, *36*, 1387.
16. Turner, S.R.; Walter, F.; Voit, B. I.; Mourey, T. H. Macromolecules **1994**, *27*, 1611.
17. Hamb, F.L. J. Polym. Sci. **1972**, *A-1*, *10*, 3217.
18. Cantrell, G. R.; McDowell, C. C.; Freeman, B. D.; Noel, C. J. Polym. Sci., Polym. Phys. Ed. **1999**, *37*, 505.
19. Bhowmik, P. K. PhD Dissertation, University of Massachussetts, 1991.
20. Lieser, G.; Schwarz, G.; Kricheldorf, H. R. J. Polym. Sci., Polym. Phys. Ed. **1983**, *21*, 1599.
21. Economy, J.; Volksen, W.; Viney, C.; Geiss, R.; Siemens, R.; Karis, T. Macromolecules **1988**, *21*, 2777.
22. Field, N. D.; Baldwin, R.; Layton, R; Fray, P.; Scardiglia, F. Macromolecules **1988**, *21*, 2155.
23. Imasaka, K.; Nagai, T.; Yoshida, M.; Fukuzaki, H.; Asano, M.; Kumakura, M. Makromol. Chem. **1992**, *193*, 715.
24. Kricheldorf, H. R.; Jurgens, C. Macromol. Chem. Phys. **1996**, *197*, 2795.
25. Vert, M. J Mater. Sci. Mater. Med. **1990**, *1*, 123.

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