Multiphase materials with lignin: 7. Block copolymers from hydroxypropyl lignin and cellulose triacetate

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Several block copolymers were prepared from hydroxypropyl lignin (HPL) by crosslinking with NCO-terminated cellulose triacetate (CTA) of low degree of polymerization (*DP*). Copolymer films were obtained by solution casting of the uncured mixture, followed by curing. The parameters of investigation were HPL and CTA weight fractions and CTA block size. Morphological and thermal characteristics showed that all films were brittle materials with single T_g values and crystallinity even for cellulose blocks of *DP* 10. Network structure was not found to influence material properties, but crystallinity did in all compositions.

(Keywords: multiphase materials; lignin; block copolymers)

INTRODUCTION

Block copolymers have gained considerable interest in recent years because of their many unique properties[1,2]. The chemistry, architecture and location of the different blocks within a material strongly affect such properties as elastomeric behaviour, melt rheology and toughness in rigid materials. Those properties are mainly due to the coexistence of a 'hard' segment (T_m and T_g are above room temperature) and a 'soft' segment (T_g is below room temperature). The hard block acts as reinforcing site within the material, while the soft block confers the material its elastomeric nature. It is with the development of polyurethanes that block copolymers achieved pre-eminence.

Hydroxypropyl lignin (HPL) has been used as amorphous segment in the synthesis of copolymers[3–6]; and cellulose acetate has independently been employed as semicrystalline (hard) segment of polyurethane block copolymers[7,8]. The synthesis of graft and block copolymers from cellulose acetate has been studied extensively by Stannett, Gilbert and coworkers[9–15]. Cellulose triacetate (CTA) blocks with hydroxy end-groups were described by Steinmann[16]. Difunctional CTA blocks were diisocyanate-capped and reacted with other hydroxy-terminated polymers. The second block component consisted mainly of polyesters and polyethers (i.e. poly(propylene glycol))[11–13,16]. This method helped prepare elastomeric fibres[16] and biodegradable copolymers with high water sorption. Properties were explored in relation to cellulosic block size and its crystallization behaviour[12]. Much work aimed at improving reaction conditions such that crosslinking through excess hydroxy groups in cellulose was avoided[7,8]. This was however not completely successful, and chain branching or grafting has remained an obstacle. This is why usually only the non-cellulosic block (i.e. the polyether diol) is end-capped with a diisocyanate, and this is subsequently reacted with carbohydrate oligomers.

Despite considerable difficulties with the synthesis of these types of copolymers, it is possible to prepare block copolymers from cellulose acetate not only with diol polymers but also with styrene and chloroprene[17], with diisocyanates alone[18] and with block types leading to star-like block copolymers[19].

This research deals with the synthesis, characterization and properties of CTA block copolymers with HPL. Copolymer properties are to be related to such variables as block fraction and block size. It is expected that a lignin derivative (block A)–cellulose derivative (block B) block copolymer would display thermal and mechanical properties resembling similar types of materials from petrochemical sources, and obeying similar rules. The purpose of this study was, therefore, to synthesize a series of lignin–carbohydrate block copolymers in which the cellulose-derivative block dimensions were varied.

EXPERIMENTAL

Materials

Cellulose triacetate (CTA) was supplied by Eastman Kodak Co., Kingsport, TN. It had an acetyl content of 43.2%, indicating a *DS* of 2.8. Organosolv (aqueous ethanol) lignin from aspen was supplied by Biological Energy Corp., Valley Forge, PA. Hydroxypropyl lignin (HPL) was obtained from the reaction of propylene oxide with organosolv lignin. Details of HPL synthesis and of its characteristics have been reported elsewhere[20,21]. 2,4-Toluene diisocyanate (TDI) was supplied by Eastman Kodak Co. Dibutyltin dilaurate was used as catalyst, and it was supplied by Union Carbide.

CTA oligomer synthesis. Following the method of Steinmann[16], the parent CTA sample (20 g) was dissolved in a mixture of 300 ml ethylene chloride and 20 ml methylene chloride. The mixture was dried by distillation until 20 ml of distillate had been removed. At 75°C, 20 g

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1,3-dioxolane were added with stirring followed by the addition of 0.5 ml BF_3 etherate (40%). The reaction was terminated by the addition of water (variable volumes) and 0.6 ml triethylamine. After filtration, the solvent was evaporated and the yellowish powder was soaked in 2-propanol for several hours and further digested by boiling in water for 2 h. The isolated white powder was dried in an oven at 100°C. The hydroxy content of each CTA oligomer was determined by the carbanilation method[22,23] using reaction with phenyl (mono)isocyanate followed by u.v. absorbance measurement. Hydroxy equivalents per mole of CTA oligomer (*n*OH/mole) were calculated following the determination of average molecular weights ($\bar{M}_n$) either by v.p.o. (for low molecular weights) or by viscosity (for higher molecular weights).

CTA prepolymer synthesis. A solution of 0.1 g ml^{-1} CTA oligomer in pyridine, stirred at room temperature under a nitrogen atmosphere, was combined with excess TDI and heated. The mixture was precipitated into anhydrous ether, and the white precipitate formed was thoroughly washed with ether and dried under vacuum over P_2O_5. The NCO content was determined by titration with *N*-butylamine[24]. The number of NCO equivalents per mole of prepolymer (*n*NCO/mole) was calculated following the determination of M_n by v.p.o.

Copolymer synthesis. The CTA prepolymer was dissolved in 20 ml ethylene chloride and stirred vigorously. HPL and T-9 catalyst (0.1 wt %) were added, and the mixture was heated at 60°C for 1 h. Films were cast directly from a 20% solution in ethylene chloride on Teflon plates. The plates were left under the hood for 12 h to allow the solvent to evaporate slowly before curing in an oven at 100°C for 12 h. The films were kept in a vacuum desiccator for one week before testing.

Methods

Thermal analysis. Differential scanning calorimetry (d.s.c.) was performed on a Perkin–Elmer DSC-4 system equipped with a Thermal Analysis Data Station (TADS) using the scanning auto-zero accessory. The sample (5–10 mg) was heated under nitrogen at a rate of 20°C min^{-1}. The glass transition temperature (T_g) was defined as one-half the change in heat capacity that occurs over the transition of the second scan. CTA was heated to the melting point at 100°C min^{-1}, quenched to 30°C at 200°C min^{-1} and scanned by heating at 20°C min^{-1}. The HPL sample was heated to 160°C at 100°C min^{-1}, quenched at 200°C min^{-1}, and scanned at 20°C min^{-1}.

Swelling. Swelling studies were performed in dimethylformamide (DMF). The material was mixed with solvent and left standing for 5 days before weighing the amount of swollen material. The insoluble component was left to dry for several days in a desiccator until constant weight was obtained. Weight gain upon swelling and sol fraction were calculated.

X-ray scattering. Morphological characteristics of the films were studied by wide-angle X-ray scattering (WAXS) on a Phillips diffractometer using a Cu Kα source in the usual manner. Sample thickness was about 0.010 inch (0.25 mm).

RESULTS AND DISCUSSION

Block copolymer synthesis

Cellulose acetate component. The synthesis of CTA blocks with low degree of polymerization (*DP*) may employ either sulphuric acid and water, or 1,3-dioxolane and boron trifluoride etherate (as catalyst) in a mixture of ethylene chloride–methylene chloride and water[16]. Steinmann[16] has demonstrated that the first method, even though it requires shorter reaction times, causes deacetylation and hydrolysis of acetyl groups. This results in blocks having higher hydroxyl content. The second method was therefore selected even though it has other weaknesses such as acetyl migration, redistribution and repolymerization.

Parent CTA hydrolysis (*Figure 1*) produced rapid depolymerization to a constant *DP* of ~10. Three oligomeric fractions were isolated after 20, 32 and 46 h of reaction time, and these were designated as C20, C32 and C46 (*Table 1*). The characteristics of the corresponding TDI-capped prepolymers (*Table 1*) revealed that, while some of the hydroxy groups had remained unreacted, C46 had dimerized. Two block sizes were produced, one with

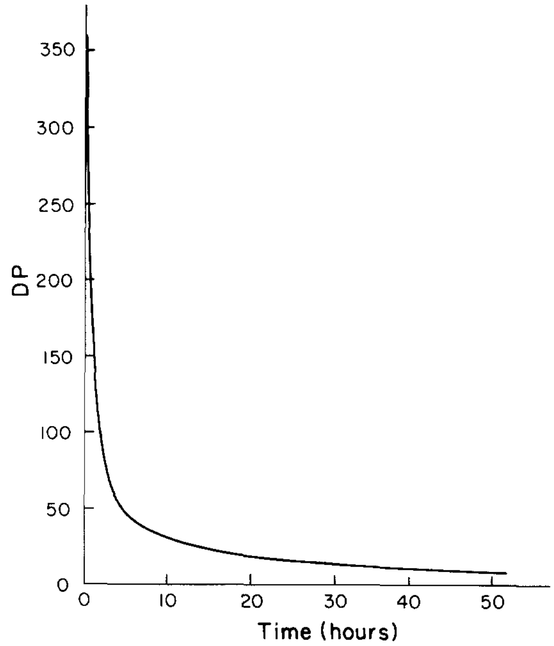

Figure 1 Relationship between degree of polymerization (*DP*) and time of depolymerization of parent CTA. (Note: *DP* was computed from viscosity measurements at 25°C by using the relationship $DP = 147[\mu]^{1.2}$; the solvent was CH_2Cl_2/MeOH 9:1 by weight)

Table 1 Characteristics of CTA block components

	Oligomer/prepolymer			
Structural features	Parent CTA	C20	C32	C46
CTA oligomers				
Hydrolysis time (h)	0	20	32	46
$\bar{M}_n$	100 000	5200	2600	3000
DP	355	20	10	10–11
*n*OH/mole	50	2.9	1.9	1.9
OH (%)	0.86	0.95	1.23	1.05
CTA prepolymers				
$\bar{M}_n$	n.a.	5500	3600	6500
DP	n.a.	20	12	20
NCO (%)	n.a.	1.72	1.49	1.27
*n*NCO/mole	n.a.	2.2	0.9	1.96

DP 12 (i.e. C32) and two with *DP* 20 (i.e. C20 and C46). Only the larger blocks were found to be difunctional and thus potential crosslinking agents; the *DP* 12 block (C32) had mono-NCO functionality. Several complex competing side-reactions seem to occur during TDI end-capping, and these make the tailoring of perfectly difunctional NCO-capped CTA blocks of predetermined size difficult.

TDI was selected as diisocyanate because the *ortho*-NCO group becomes 10 times less reactive upon reaction than the *para*-NCO group, and this conveniently prevents chain extension[25–27]. Rahman and Avny[26] prepared isocyanate-terminated poly(ethylene oxide) (PEO) segments (for the synthesis polyurethane block copolymers) by reaction with TDI in benzene under an argon atmosphere at 25°C for 1 h. The selectivity between the two NCO groups was reported to decrease, and chain extension may occur, when using a catalyst (dibutyltin dilaurate). D.s.c. thermograms (*Figure 2*) reveal endothermic peaks characteristic of melting at 274 and 264°C for C20 and C32, respectively. This indicates that even severely depolymerized CTA remains crystalline. An endothermic transition responsible for T_g is discerned at 137 and 173°C for C32 and C20, respectively. The endothermic peak at 70°C observed for C20 may possibly be attributed to conformational reorganization of the glucose ring. (It was also observed for the parent CTA.) This does not occur in C32, probably because the *DP* is too low. The values for T_g, T_m and ΔH_m for the various prepolymers (*Table 2*) indicate variations in relation to block size and chemistry. The effect of TDI, and the reduction in molecular weight, contribute to a reduction in T_g. The lower values of T_g and T_m observed for C32 as compared to C46 and C20 can be attributed to a decrease in *DP*. Surprisingly, the heat of fusion ΔH_m of C32 is higher than that of C20 and C46 despite its lower *DP*.

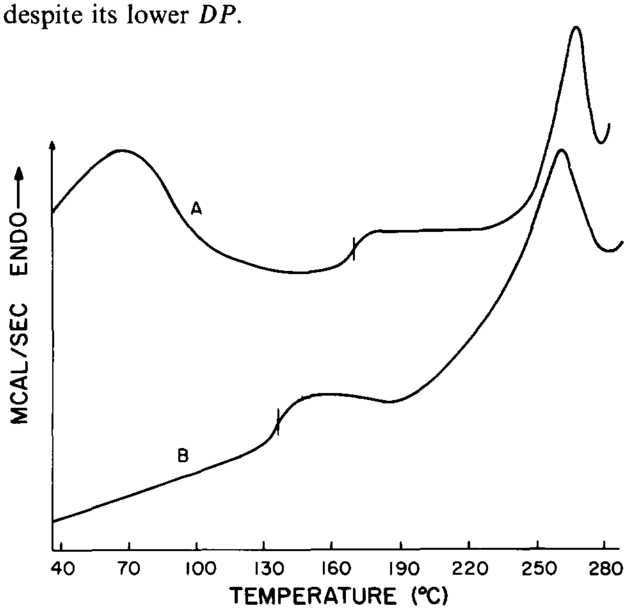

Figure 2 D.s.c. thermograms of (A) C20 and (B) C32 prepolymer

Table 2 D.s.c. results of CTA prepolymers

Prepolymer	T_g (°C)	T_m (°C)	ΔH_m (cal g^{-1})
Parent CTA (*DP* 355)	184	296	5.6
C32 (*DP* 12)	137	264	3.54
C20 (*DP* 20)	173	274	2.3
C46 (*DP* 20)	174	274	2.4

Table 3 Formulation parameters of block copolymers

Copolymer	Molar OH/NCO ratio	HPL content (%)
Series P32[a]		
P32067	6.7	40
P32025	2.5	20
P3201	1	10
P32005	0.5	5
Series P20[a]		
P2012	12	55
P2010	10	50
P2008	8	45.5
P2006	6	37.6
P2004	4	28.7
Series P46[a]		
P4612	12	50
P4610	10	45.5
P4608	8	40
P4606	6	33.3
P4604	4	25

[a] The first two digits designate prepolymer source, and the last two digits indicate OH/NCO ratio

Hydroxypropyl lignin component. Hydroxypropyl lignin (HPL) has been described previously[20,21]. The HPL block characteristics indicated a hydroxy content (by titration) of 6.1%, a number-average molecular weight $\bar{M}_n$ (by v.p.o.) of 1600 g mol^{-1} and a T_g (by d.s.c.) of 80°C.

Block copolymerization. Block copolymers were obtained by mixing the CTA prepolymer and HPL in the presence of catalyst in ethylene chloride solution. Films were obtained by casting the mixture from solution in accordance with previous work[3–6]. Formulation parameters for the block copolymers (*Table 3*) include CTA prepolymer source and molar OH/NCO ratio (i.e. weight fraction of blocks). For example, the sample designated P4612 is the copolymer made from C46 prepolymer with a molar OH/NCO ratio of 12. The selection of HPL content was dictated by stoichiometry. Because of its high OH functionality, HPL content ranged from 5 to 55% (*Table 3*). This suggests that crosslinking was generally minimal. Since the number of NCO equivalents of the CTA prepolymers was low compared to the number of OH equivalents of HPL, the molar OH/NCO ratios of all samples were greater than 1 (*Table 3*).

Block copolymer properties

All copolymer films were clear, glassy (highly brittle) solids unqualified for dynamic mechanical thermal analysis (modulus and tan δ) or stress–strain testing. However, thermal properties and network morphology were tested by d.s.c., swelling and wide-angle X-ray scattering.

The d.s.c. thermograms (*Figure 3*) reveal the presence of glass transitions (T_g), of broad crystallization peaks (T_c) and of a melt endotherm (T_m). All curves have identical shape except that the transitions are shifted. The experimental values of T_g, T_m and heats of fusion ΔH_m (i.e. area under the melt endotherm) for each copolymer (*Table 4*) reveal several consistent relationships.

The d.s.c. thermograms (*Figure 3*) exhibit single T_g values between 100 and 135°C, and thus between the T_g values of the two individual homopolymers. That T_g and HPL content are related, with T_g decreasing as HPL

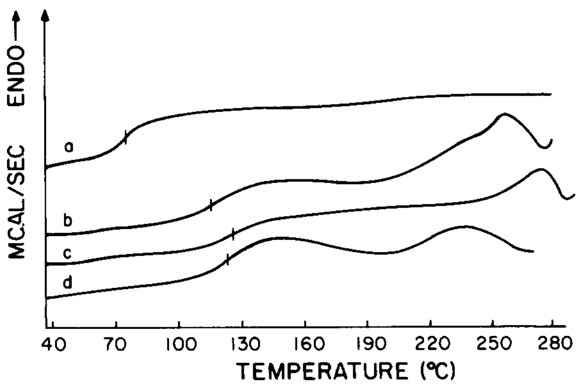

Figure 3 D.s.c. thermograms of (a) hydroxypropyl lignin (HPL), (b) copolymer P4608, (c) copolymer P2008 and (d) copolymer P3201

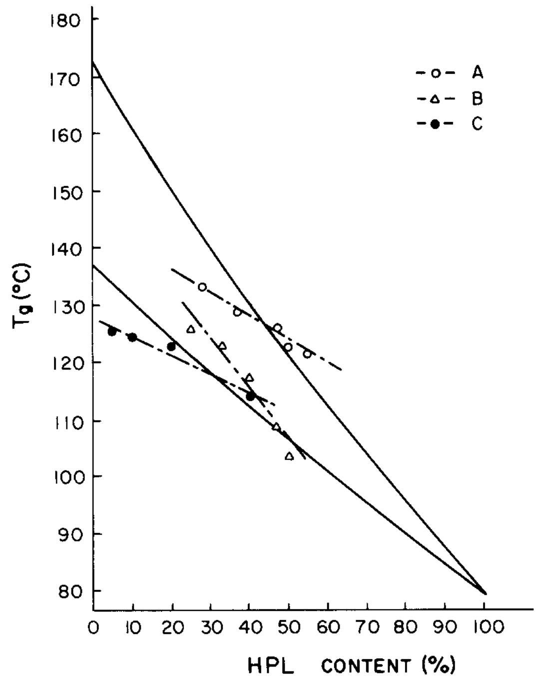

Figure 4 Relationship between HPL content and T_g of CTA copolymers of (A) series P20, (B) series P46 and (C) series P32

content increases (*Figure 4*), is due to differences in CTA block size. If this size decreases, T_g decreases. A comparison between experimental results and those predicted by the Fox[28] equation (*Table 4* and *Figure 4*) reveals a consistent variation between experimental and theoretical results, which may account for the non-randomness in the copolymers. This agrees with a block rather than a random copolymer structure, and with the existence of crystallinity.

It is recognized that the copolymers are composed of three components: amorphous lignin, amorphous cellulose and crystalline cellulose. In this system, the two closely associated amorphous components exhibit a single T_g, while the crystalline cellulose separates into crystalline domains. This agrees with reports on related block copoly(ether ester) materials[29]. Single T_g behaviour may, however, also be due to the short size of the two blocks, and two separate T_g transitions may emerge if block sizes become greater. The interaction between lignin and cellulose derivatives in polymer blends has been the subject of prior investigations[30], and this has established a remarkable degree of compatibility between the two amorphous components. The unexpected failure of (solution-cast) cellulose acetate butyrate/lignin blends to display dual T_g transitions, even when two-phase morphology was indicated by microscopy, was tentatively explained by the development of a supermolecular (possibly liquid-crystal mesophase) structure[31]. A similar binary interaction may provide an explanation for the observed single T_g transition in CTA/lignin block copolymers.

Experimental T_m values of copolymers were observed in the ranges 258–282°C and 254–258°C for the copolymers of the series P20 and P46, respectively, and between 246 and 252°C for the series P32. These melting temperatures, influenced by block size and other factors, are lower than the T_m values of the corresponding prepolymers (*Table 2*) as well as that of the parent CTA. This is not unusual considering the introduction of lignin and diisocyanates. The crystallization behaviour of block copoly(ether ester) has recently demonstrated[29] that the T_m of the individual components remained unaffected if the crystallizable segment length exceeded 12 units. This supports the absence of significant variations in the T_m of CTA/HPL copolymers, since the length of the cellulose segments exceeds the maximum length beyond which T_m does not vary.

Since the crystallization behaviour of the copolymers is attributed to the CTA block, heat of fusion and cellulose content must be related. This relationship (*Figure 5*) shows that the heats of fusion are higher for the copolymers having longer CTA segments (i.e. P20 and P46 series) than for those with shorter ones (i.e. P32 series). The extrapolation to 100% CTA content yields values for ΔH_m which agree with those obtained by d.s.c. on the prepolymers (see *Table 2*). Except for the 100% composition, the copolymers with CTA segments of *DP* 20 (i.e. those of the series P20 and P47) are more crystalline than those composed of *DP* 10 blocks. This can be explained by the fact that the shorter cellulose chains mix better with HPL, since the two low-molecular-weight components have less tendency to restrict each other's mobility. Therefore, the occurrence of phase separation is minimized, and this reduces crystallinity. The opposite effect is observed with the two copolymer

Table 4 Thermal copolymer characteristics from d.s.c. experiments

Copolymer	T_g (°C) experimental	T_m (°C)	ΔH_m (cal g^{-1})	T_g (°C) theoretical[a]
Series P32				
P32067	113	252	0.5	112
P32025	123	250	0.5	124
P3201	125	239	0.8	130
P32005	126	246	1.0	133
Series P20				
P2012	122	282	0.5	117
P2010	122	273	0.8	121
P2008	127	274	1.2	126
P2006	128	274	1.6	133
P2004	133	258	1.6	142
Series P46				
P4612	104	258	1.0	
P4610	110	258	1.3	
P4608	117	255	1.4	
P4606	123	258	1.6	
P4604	126	254	1.7	

[a] Theoretical values were calculated from the model of Fox[28]

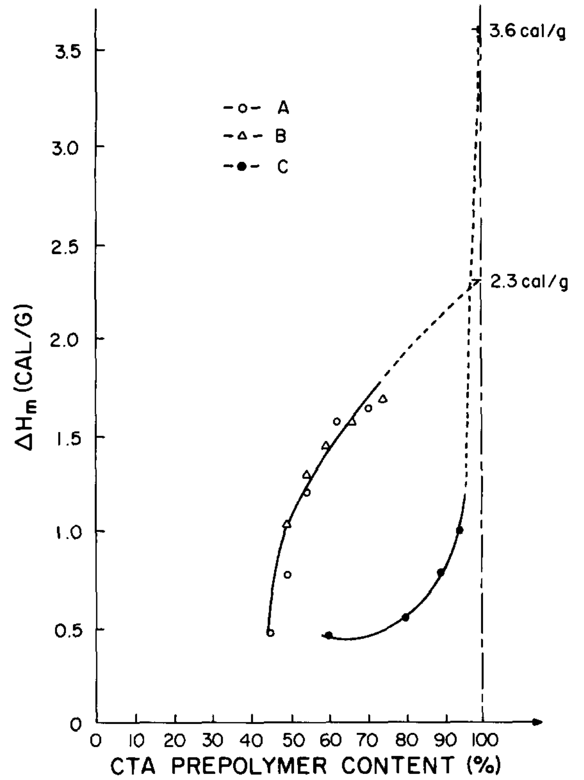

Figure 5 Relationship between heat of fusion ΔH_m and CTA prepolymer content for copolymer series (A) P20, (B) P46 and (C) P32

series having longer CTA segments, which display a better developed crystalline phase.

Heat of fusion, and consequently degree of crystallinity, increases with CTA content (*Figure 5*). This may suggest that network structure is not strongly developed. To test this hypothesis the swelling properties were examined. The results (*Table 5* and *Figure 6*) reveal sol fractions between 40 and 90% which are consistently related to CTA content. The high degree of dissolution confirms the low degree of crosslinking in general, and the almost total absence of network structure in the P32 samples containing monofunctional CTA blocks of small *DP*. The sol fraction decreases slightly as CTA content increases. This can be explained either by increased crosslinking or by increased crystallinity.

The observation of crystallinity is surprising because the copolymers consist of very short segments that form a (more or less) crosslinked network structure with very low segmental mobility. It is, however, not without parallels. Mezger and Cantow[17] reported that the high tendency of cellulose triesters to crystallize facilitates phase separation, and Feger and Cantow[19] observed phase separation in star block copolymers with CTA. It must, therefore, be suspected that the synthetic method employed favours phase separation in the amorphous–crystalline block copolymers, which have the potential to crosslink but where the degree of crosslinking remains low. The formation of crosslinks is minimized (a) because the NCO content of the prepolymers is low, and (b) because NCO groups are concentrated at the end of the cellulose chains, allowing crystallization to dominate.

Small-angle X-ray scattering (SAXS) failed to produce conclusive results regarding the multiphase morphology of the copolymers. Wide-angle X-ray scattering (WAXS), however, revealed scattering patterns with sharp, concentric, continuous and uniform rings characteristic of a crystalline phase (*Figure 7*). (The external halo can be attributed to the scattering of the amorphous component.) The intensities of the concentric rings are shown to remain practically constant in relation to CTA content and block size. Only the P4604 preparation exhibits a much more resolved scattering pattern, with more distinct rings, and this agrees with the high ΔH_m value (i.e. 1.68 cal g^{-1}) observed with this sample compared to the other copolymers (*Figure 5* and *Table 4*). Therefore, P4604 is recognized as the copolymer having the highest degree of crystallinity. Other studies on the crystalline structure of cellulose[32–34] have shown that an X-ray pattern of continuous, concentric and uniform rings is produced by an aggregate of small grains or micelles in random orientation. The sharpness of the rings is related to micelle size. The diameter of the diffracting particles was found to lie between 10^{-3} and 10^{-6} cm if the rings are sharp and uniform[34]. If larger than 10^{-3} cm, the diffraction pattern becomes dashed and spotted as would be expected for larger single crystals. If smaller than 10^{-6} cm, the rings become broader in proportion to decreasing particle size. Applied to CTA, which is known for its high crystallinity[17,35], the WAXS results allow the conclusion that the copolymer is composed of a randomly oriented crystalline structure. The size can be estimated to be larger than 600 Å. This value seems high for short

Table 5 Results from swelling experiments

Copolymer	CTA prepolymer content (%)	Weight gain (%)	Sol fraction (%)
Series P32			
P32067	60	392	93
P32025	80	150	92
P3201	90	62	89
P32005	95	22	82
Series P20			
P2012	45	700	51
P2010	50	724	55
P2008	54.5	600	55
P2006	62.4	516	45
P2004	71.3	396	40
Series P46			
P4612	50	929	61
P4610	54.6	951	59
P4608	60	852	56
P4606	67	716	48
P4604	75	663	43

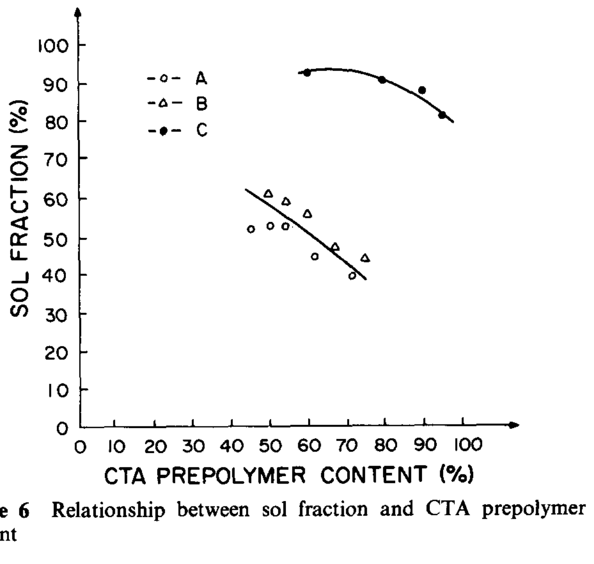

Figure 6 Relationship between sol fraction and CTA prepolymer content

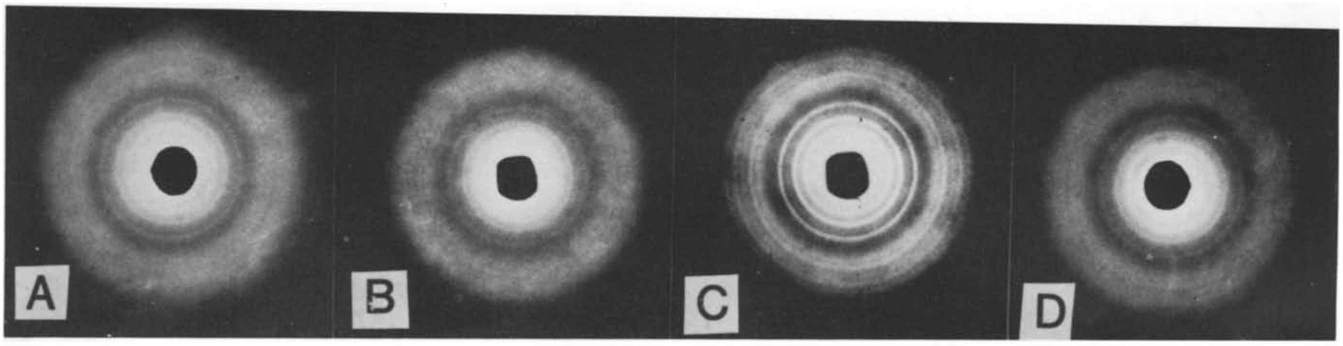

Figure 7 WAXS results of (A) copolymer P3220, (B) copolymer P3240, (C) copolymer P4604 and (D) copolymer P4608

cellulose segments and may be explained by the better tendency of short chains to orient compared to high-molecular-weight chains. This agrees with the absence of a distinct SAXS pattern, which detects domains of less than 140 Å in size.

When examined through a microscope equipped with a polarizing lens and a hot stage, transparent (crystalline) zones disappear upon heating to the melting point but do not reappear when annealed between 150 and 200°C for 1 h. This observation agrees with that of Baker *et al.*[35], who failed to detect crystallization of CTA samples annealed at 150°C for 95 h. This supports the high intermolecular forces existing in CTA which, at this temperature, restrict chain rotation. It can be assumed that not only are HPL and CTA linked together covalently, but they also are closely associated through secondary intermolecular forces. This explains why the close association between the two blocks in the amorphous phase produces single T_g behaviour.

CONCLUSIONS

Copolymers from NCO-capped cellulose triacetate (CTA) oligomers and HPL were synthesized with a range of compositional parameters. The synthesis was limited by difficulties encountered in the depolymerization of CTA to cellulose blocks of a target size. The following relationships have been observed.

Copolymer properties are dictated by the glassiness of the individual components, and by the crystallization of CTA at all *DP* levels.

T_g values are very near the values predicted by the Fox relationship.

Properties are not substantially affected by network architecture since sol fractions are above 40%.

Phase separation between an amorphous, closely associated HPL/CTA component is dictated by covalent bonds and by intermolecular fources, and by a crystalline phase composed of randomly oriented, organized micelles.

The size of the crystalline domains is estimated to be ~600 Å.

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