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A review on aromatic poly(ester-carbonate)s and transesterification resistant polyesters

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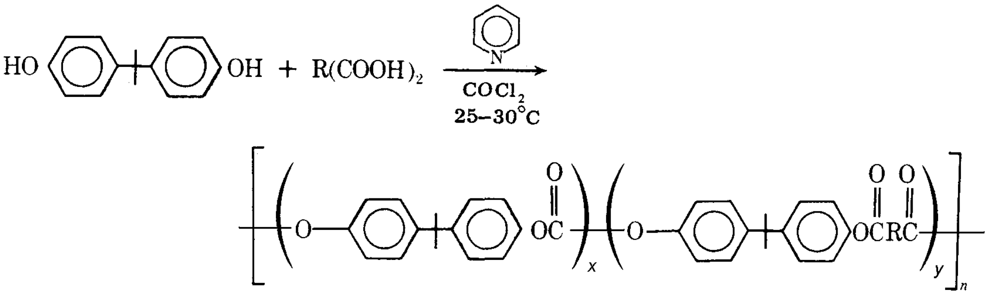
Abstract: The review discusses poly(ester-carbonate)s (PECAs for brief), their production, characterization and their use. Great emphasis is on their production *via* ester-carbonate exchange and in particular on the copolymer obtained when mixing and heating poly(butylene terephthalate) (PBT for brief) or poly(ethyylene terephthalate) (PET for brief) together with poly(bisphenol A carbonate) (PC for brief). Some notes are added on PECAs with long polyester and /or long polycarbonate blocks and for the case of "transesterification resistant" polymers i.e. when the production of random copolymers *via* ester-carbonate exchange is impossible under ordinary conditions.

Introduction

Poly(ester-carbonate)s , PECAs for brief, are copolymers in which ester and carbonate units are both found along the chain and many patents have been issued on their synthesis and applications [1-7]. In 1965, Goldberg [1] patented a process for the production of PECAs using phosgene, bisphenol-A and adipic acid (actually the dichloride).



The process is not limited to the production aromatic-aliphatic PECAs. In fact, replacing the adipic acid with terephthalic (or isophtalic) acid, the process yields fully aromatic PECAs. The latter copolymers are also referred to as poly(aryl ester-carbonates) and they have attracted some attention since they combine the desirable properties of aromatic polycarbonates and polyarylates [8-12]. More in detail, polycarbonate resins are tough, rigid and easily processable, but have quite low softening temperatures. On the other hand, polyesters exhibit two desirable properties, namely good processability and high softening temperatures, but they lack a high "notched" impact resistance. Surprisingly, the synthetic route which uses phosgene (a highly poisonous compound) has not become old-fashioned, probably because it is very efficient. Fully aromatic PECAs can be alternatively produced using interfacial polymerization [7] or using diphenyl-carbonate.

PECAs are indeed copolymers and the theory predicts that their mechanical properties depend on the composition i.e. on the relative abundances of PC and polyester (PET or PBT). Moreover, mechanical properties change with sequence i.e. how PC and PET units alternate along the chain. In almost perfectly alternating PECAs, bisphenolA_terephthalate units are ubiquitous; the presence of two consecutive ester or carbonate units is very rare. Bosnyak et al. described a process yielding perfectly alternating PECAs [11, 12].

In the early eighties, Devaux and coworkers [13] proposed an alternate synthetic route for PECAs based on melt-mixing of two homopolymers. They claimed that the resulting copolymer is initially “blocky” i.e. it possesses long polyester and polycarbonate blocks and then it tends to become a random copolymer. They reacted poly(butylene terephthalate) and poly(bisphenolA carbonate) in the melt at 290 °C [14-15]. Further in their studies, they [16-17] reacted poly(ethylene terephthalate) and poly(bisphenolA carbonate) in the melt at 280 °C. In this case, the system eliminates CO_2 and also ethylene carbonate. Thus, the resulting copolymer is actually a poly(ether-ester-carbonate).

In a similar manner, Lee and Woo [18] synthesized a poly(ester carbonate) by reacting PC with poly(trimethylene terephthalate). Zhang et al [19] obtained a PECA by reacting PC with a copolyester with units of ethylene terephthalate and epsilon-caprolactone. The choice of using a copolymer was probably dictated by the fact that, when PC is heated with poly(epsilon-caprolactone) alone, annoying side reactions occur and chains in the reaction mixture become branched and eventually crosslinked [20]. Wei and Ho [21] synthesized a poly(ester carbonate) reacting PC with copoly(oxybenzoate -p-terephthalate) (a random liquid-crystalline polyester) at 260 °C in vacuum. Kollodge et al [22] obtained small amounts of PECA by heating a blend of PC and poly(2-ethyl-2-methylpropylene terephthalate) at 280 °C for relatively short times. An interesting variant is letting PC react with PET (or another polyester) in the solid state (instead of in the melt) [23].

PECAs have been analyzed using a variety of techniques [24-25]. Thermal methods are very useful. The glass transition temperature (T_g) of the PECAs falls invariably in the region between 423 °C (the T_g of PC) and the T_g of the polyester. Size Exclusion Chromatography (SEC) yields M_n, M_w and the ratio M_w/M_n [23-24]. The use of spectroscopic method such as infrared (IR) and Nuclear-Magnetic-Resonance (NMR) is widespread for PECA analysis [24-25]. In the IR spectrum, the bands due to carbonate and the ester groups are well resolved and thus the composition (ester/carbonate ratio) is readily obtained from the ratio of the areas beneath the two bands. In the case of PECAs obtained from monomers, the first technique (which is probably less demanding in terms of effort) may suffice for characterization. However, in the case of PECAs obtained by heating two homopolymers, there is a need for highly accurate characterization tools. In fact, the measurement of the reaction yield is very difficult. Furthermore, the measurement of copolymer’s composition can be biased by the presence of unreacted homopolymer chains.

In order to monitor the reaction, one can monitor the changes of the number average lengths $<n_A>$, $<n_B>$ (here A and B stand for ester and carbonate units, respectively). In fact, the length of long AAAA and BBBB blocks is expected to fall as the reaction proceeds. The degree of randomness, B_{rand}, is a very popular quantity too [24-25].

Devaux and coworkers recorded the ^{13}C-NMR spectra of PC/PBT blends reacted at 290 °C for different times [14-15]. The spectra displayed a series of peaks in the region 60-160 ppm, the most notable peaks falling at 66-69, 119-120, 128-130, 147-148 ppm . The task of extracting the quantities $<n_A>$, $<n_B>$ and B_{rand} from the NMR spectrum using the methods developed (among others) by Bovey and by Coleman-Fox turned out to be difficult (the full treatment can be found elsewhere [26] and it is lengthy indeed). For this reason, they developed a fully innovative method. They noted that the repeat unit of PBT and of PC can be ideally split in two parts and thus they introduced four "half-monomers". In the case of of PC/PET, the NMR spectrum of the reacted blend is richer in peaks and they are therefore more difficult to interpret than the previous ones. Nevertheless, they were able to extend the previous formulas (valid for 4 half-monomers) by considering 5 half-monomers [16-17]. The formulas developed are quite simple in all cases, the half-monomer method enjoyed good success and it was applied to interpret the NMR spectra of virtually all PECAs.

Mass spectrometry can be used for PECA characterization too. In SIMS, a narrow ion beam (usually made of Ga^+ ions, the beam diameter of a couple of microns) hits the sample, and secondary ions (coming from the sample) are detected. Figures 1b and 1c report SIMS mass spectra for a PC-PET blend heated for 10 and 60 minutes respectively, along with SIMS mass spectra for PC (Figure 1a) and for PET (Figure 1d) [27]. It can be seen that spectra 1b and 1c display a larger number of peaks with respect to the corresponding homopolymer, hinting that the two homopolymer do react and that a PECA copolymer is formed. The additional peaks are seen at m/z= 359, 403, 447,491. They were assigned [14] to ions in which terephthalic and bisphenol-A moieties are chemically bonded, thus confirming the occurrence of the transesterification reaction.

Despite PECAs possess formidable properties, industry does not consider them appealing and the use of PECAs is not widespread. As a matter of fact, researchers soon realized that it is possible to produce resins with the above properties by simply creating a PC–PBT or PC–PET mixture and processing it in an extruder. Most commercial blends are 50/50 in weight and therefore they deviate slightly from equimolar blends. These blends possess two clear advantages over copolymers, namely the three homopolymers (PC, PET and PBT) can be readily found on the market and changes in the formulation can be performed much more easily than corresponding changes for copolymers. Commercial blends of PC and of PBT include Sabre ® 1600 from the Dow Chemical Company, Ultrablend® KR from BASF, Xenoy ®, from General Electric Plastics, Makroblend ®, from Bayer and Stapron® E from DSM . These blends are mainly used in the automotive industry for body panels. Santos and Guthrie [28] recently published a review on PC-PET blends. Four types of additives are included in the blend formulations, namely pigments, thermal stabilizers, rubbers called "impact-modifiers" (the best ones are made of polystyrene plus polybutadiene plus polymethylmethacrylate) and transesterification reaction inhibitors (mainly phophorous componds). The need for the last additive is due to the fact that, when the mixture is processed in the extruder, ester-carbonate exchange reactions occur and the reaction product is a PECA, which is indeed a copolymer. The theory predicts that the mechanical properties of the blend should improve. In fact, the blend morphology is made of two phases, A and B, phase A is rich in PC and phase B is rich in polyester. It is known that the PECA copolymer moves to the A-B interface, improving the adhesion and thus improving blend's properties. However, the reality is completely different. Transesterification reactions are difficult to control (one of the difficulties is related with the heating time) and the product changes from batch to batch.

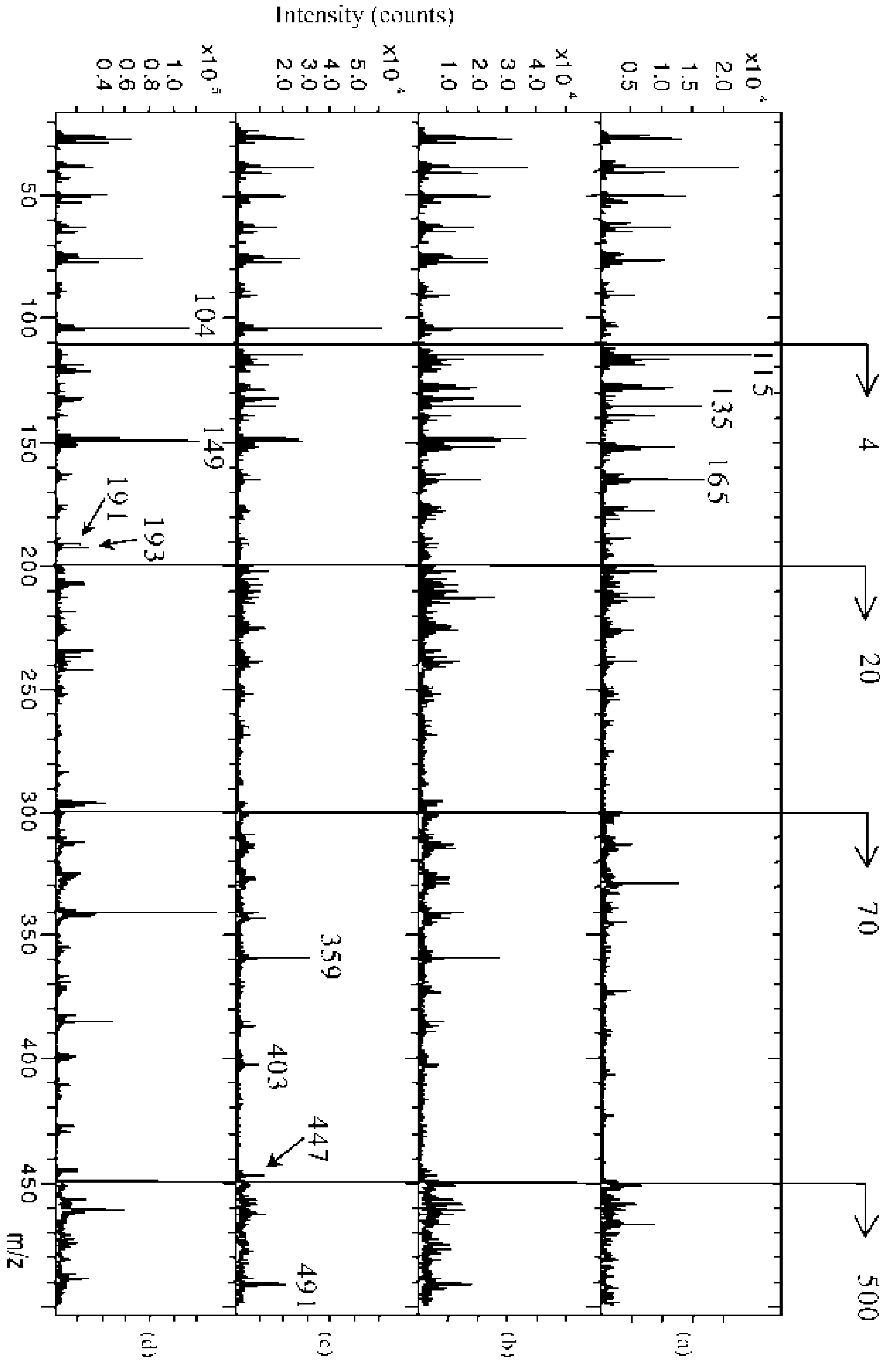


Fig. 1. SIMS mass spectra for a PC-PET blend heated for 10 and 60 minutes respectively (b) (c), along with SIMS mass spectra for PC (Figure 1a) and for PET (Figure 1d). Reproduced with permission from ref [26].

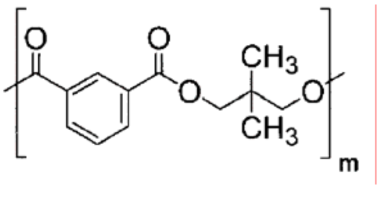
In the industry, exchange reactions are considered detrimental to blend's properties and exchange reaction inhibitors are added. Just to mention some, Cheung et al. described a phosphite inhibitor [29, 30] whereas Hamilton [31] and Tyrell [32] described a sislyl phosphate and a boric acid stabilizer, respectively.

In our laboratory, we have studied the finer details of transesterification reactions in PC-PET and PC-PBT blends. The work started with the synthesis of homopolymers with well defined end-groups, such as PC terminated with bisphenol-A on both sides or PET terminated with COOH on both sides. This task may appear trivial and not original, but this is not the case, since some polymers in the market are mixtures of chains terminated with two (or more) different types of end-groups. For instance, PC marketed by General Electrics under the name LE220 has three spectroscopic peaks, which correspond to three different types of end-groups. In our lab, the synthesis was followed by painstaking efforts to demonstrate (mainly by spectroscopic means) that all chains possess the same chain ends. By reacting these "pure" polymers, we found that end-groups have an enormous influence on the rate of exchange and that, for some end-groups, the rate of exchange was zero (or vanishingly low). Other end-groups are highly reactive, but by the use of suitable capping groups (such as methyl-esters) at chain ends, the rate of exchange returns to zero. The results show that, using capped polyesters to produce PC–PBT or PC–PET blends it is possible to avoid the use of transesterification reaction inhibitors [33, 34].

As a matter of fact, we produced a "transesterification resistant" polymer. Our claim is that it is possible to produce a whole series of "transesterification resistant" polymers by simply capping all reactive end-groups. For instance, poly(ethylene adipate) (PEA) can be mixed with PET [35]. In the PEA-PET blend, PEA can be capped with phenyl_ester groups (on both sides) to yield a "transesterification resistant" polymer.

A question arises naturally that whether someone else has ever claimed that it is possible to produce a "transesterification resistant" polymer, describing the process in detail. The answer is indeed positive. In 1966, Quisenberry [36] patented a process for the production of linear copolyesters containing long poly(ethyylene 2,5-dimethyl terephthalate) blocks (PDMT for brief) and other segmented linear copolyesters of 2,5-disubstistuted terephthalic acid. The author claims that the segmented copolyesters are stable for several hours in the melt, especially at temperatures up to 280 °C, and are thus highly suitable for processing in the melt without undergoing randomization within the time period normally required to extrude the melt polymer. It is quite apparent that Quisenberry believes the 2,5 substitution causes steric hinderance which, in turn, inhibits the transesterification reaction.

Recently, Moad, et al. [37] heated PET with poly(neopentyl isophthalate) (PNPEIS). The latter possesses a quaternary carbon (with two methyl groups) close to the ester group.



In the author’s words, PNPEIS is “transesterification resistant” due to steric hinderance. As a result, they obtained PET-PNPEIS multiblock copolymers.

It must be pointed out that similar to the case of PDMT by Quisenberry, the author's conclusion concerns ester-ester exchange. It would be interesting to see if PNPEIS or PDMT are "transesterification resistant" also for ester-carbonate exchange. More in detail, using polycarbonate and PNPEIS or PDMT to produce a PC– PNPEIS blends (or PC– PDMT blends), is it possible to avoid the use of transesterification reaction inhibitors? Does ester-ester exchange resistance imply ester-carbonate exchange resistance? To the best of our knowledge, no experiments have been performed to answer this question.

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