Analysis of melt copolymers

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Melt copolymer chains are the main (most abundant) reaction product obtained when heating a blend of two (or more) condensation polymers (such as polyester + polycarbonate or polyester + polyamide or polyester + polyester) in which exchange reactions occur. In fact, during the melt-mixing reaction, an AB copolymer is formed and, as a consequence, the sample is a complex mixture made of three components or simply “parts”, referred to as Z1, Z2 and Z3, where Z1 and Z2 are the parts for unreacted homopolymers (A and B), whereas Z3 is the part for the copolymer. In this paper, it is shown that matrix-assisted laser desorption/ionization mass spectrometry (and mass spectrometry in general) can be used to monitor the yield of the reactive blending reaction, \( Y_R \), by measuring the amount of unreacted homopolymer (Z1 and Z2). In order to allow for comparisons, the paper also discusses conventional methods for measuring Z1 and Z2, such as liquid chromatography and nuclear magnetic resonance.

Keywords: MALDI, polycarbonate, polyester, Nylon, reactive blending, randomness, block copolymer

Introduction

The topic of exchange reactions in condensation polymers is vast and reviews covering the entire topic, or parts of it, have been published.\(^1\)\(^–\)\(^4\) Binary polymer melts are obtained heating binary polymer mixtures above the melting temperature, \( T_m \), which is often above 200°C. In some binary polymer melts (for example, polyester–polyester, polyester–polyamide, polyester–polycarbonate and polyamide–polyamide) exchange reactions occur. Depending on the chemical groups found along the macromolecular chain, various types of exchange reaction in polymers occur, namely ester–ester exchange,\(^5\)\(^–\)\(^8\) ester–carbonate exchange,\(^9\)\(^–\)\(^15\) carbonate–carbonate exchange,\(^16\) amide–ester exchange,\(^15\)\(^–\)\(^22\) amide–carbonate exchange\(^23\)\(^–\)\(^27\) and amide-amide exchange.\(^28\)\(^–\)\(^33\) When the blend is heated, the two homopolymers can react together and form a copolymer. The above process can be described as follows

\[
\text{AAAAAAA} + \text{BBBBBB} \rightarrow \text{AAABBBBB} + \text{AAAAABBB} \quad [1(a)]
\]

The copolymer has initially long AAAAA and BBBB blocks but, as the reaction goes on, the length of the blocks decreases and it becomes random. This second process can be described as follows

\[
\text{AAAAABBBBB} \rightarrow \text{AAAABBBBAA} \quad [1(b)]
\]

Most condensation polymer blends are incompatible at room temperature. In fact, a phase separation quickly occurs in the blend, with A-rich and B-rich phases. The dimension of these two phases can be characterized by a “phase average diameter” (PHAD). Above the melting temperature, the segmental mobility is high and the blend is compatible. However, once the blend is cooled, two phases are generated and PHAD increases slowly with time, which implies that the blend is unstable. Phase separation must be avoided, otherwise the blend’s characteristics are utterly depleted. In order to overcome (at least in part) this drawback, one can add a compatibilizer. The latter are usually interfacially-active copolymers (for instance block or graft copolymers) which possess at least two different types of segment and each type is capable of specific interactions with one of the blend’s components. The action of a compatibilizer can be depicted as follows. There are two phases (I and II) separated by a phase boundary. The compatibilizer joins the two phases, since it lies partly in phase I and partly in phase II. Thanks to the compatibilizer, the overall energy of the blend is reduced and this has benefits on the mechanical properties. In some cases, one uses macromolecular compatibilizers that are totally different from the blend’s component. In the case of condensation copolymers, however, this strategy has a most evident shortcoming. In fact, condensation copolymers are often used as engineering thermoplastics and high compatibilizer concentrations must be avoided, otherwise the presence of additional repeat units may cause unwanted effects. Vice versa, it is quite apparent that the best compatibilizer for a blend of A + B is an AAAAABBBBB block.
copolymers. In fact, the system will evolve in such a way as to minimize its overall energy and it is intuitive that AAAA blocks will lie in phase I and BBBB blocks will lie in phase II. Furthermore, the best compatibilizers are those which have a relatively high molar mass so that the average length of AAAA blocks is high enough to form entanglements in phase I. It is apparent that the exchange reaction depicted in Equation [1(a)] yields a block copolymer which is ideally suited to act as a compatibilizer. Researchers in the field are constantly trying to obtain improved polymer formulations. Obviously, a prerequisite for improvement is that the products obtained by the exchange reaction must be carefully characterized.

The formation of copolymers in blends by exchange reactions has been studied theoretically. Kotliar considered the exchange reaction as a two-step process. Firstly, S scissions occur (i.e. S bonds are cleaved) and in a second step, S chain ends are joined together. The quantity, S, increases with the reaction time, t_{exc}, and, for systems in which the rate of exchange does not vary too much, it is proportional to S. Kotliar considered two cases, referred to as case I and case II, which correspond to direct interchange and to end-group exchange, respectively. Case II is more complex, since one must consider two possibilities, namely when A end-groups attack B and when B end-groups attack A.

Kotliar’s model yields analytical formulas for the time-variation of the abundance of chains of types A_BB, A_BA, A_A, and W(A), W(A–), W(–A–), which represent the weight fraction of homopolymer A, the weight fraction of A end-segments and the weight fraction of A middle-segments, respectively.

The model also predicts the time-variation of the copolymer yield, Y_{cop}. This quantity is important, since it equals the homopolymer-to-copolymer conversion and, by its knowledge, the formation of copolymer in homopolymer blends can be precisely characterized. Furthermore, the abundance of molecules remaining unaltered (i.e. unreacted molecules), Y_{un}, is easily derived, since it is given by Y_{un}=(1–Y_{cop}). The reader may think that Y_{un} decreases quickly and that it becomes that negligible at intermediate stages of the exchange reaction. The second guess is false. In fact, the model predicts that Y_{un} remains at a non-negligible level even after long reaction times.

In order to monitor the reaction, one can measure the number of average lengths &lt;nA&gt; and &lt;nB&gt; of AAAA and BBBB blocks. The degree of randomness, B_{ran}, is a very popular quantity and it can be estimated using the formula: B_{ran}=2–k_{1}–k_{2}, where k_{1}=1/&lt;nA&gt; and k_{2}=1/&lt;nB&gt;.

Three interesting quantities for characterization purposes are Z1, Z2 and Z3, where Z1 and Z2 are the weight fractions of the unreacted homopolymers (A and B) and Z3 is the weight fraction of the copolymer. It is customary to monitor the yield of the reactive blending reaction, Y_{R}, using a relation based on the reaction depicted in Equation [1(b)] above, namely Y_{R}=B_{ran}. The following equation can be put forward: the definition of yield is not a natural extension of the definition which is found in physical-chemistry textbooks (which holds for bimolecular reactions, etc.). The objection is, in our opinion, formidable. An alternative relationship [based on Equation [1(a)]] is Y_{R}=1–Z1–Z2, which states that the yield can be obtained by subtracting the “part” which has not reacted from the total. In this paper, it is shown that matrix-assisted laser desorption/ionization (MALDI) (and mass spectrometry in general) can be used to measure the amount of unreacted homopolymer (Z1 and Z2). In fact, since the discovery, in the early nineties, that polymers can be ionized by MALDI in a fashion similar to proteins and other biopolymers, MALDI is rapidly becoming a standard tool in polymer characterization. The technique has also been applied to the analysis of copolymers obtained by various synthetic routes.

In order to allow for comparisons, we must also discuss conventional methods for measuring Z1 and Z2. This is done in the following section.

Conventional methods for measuring the amount of unreacted homopolymer

Various techniques can be used to monitor the cited quantities. The components present in a crude reaction mixture can be separated by fractionation (also referred to as extraction by selective solvent). As an example, a mixture of poly(bisphenol-A carbonate) (PC) and poly(butylene terephthalate) (PBT) was heated at 275°C and fractionation with dichloromethane (DCM) was used to monitor the ester–carbonate exchange reactions. It was noted that, in the initial stages of the exchange reaction, W_{sol} (the weight of the DCM-soluble fraction) falls gently with time, but after 40 minutes of reaction, it displays a sudden jump and the entire sample (made of unreacted homoA, unreacted homoB and copolymer) becomes soluble in DCM. A similar experiment was performed using a mixture of PC and poly(ethylene terephthalate) (PET) and the findings indicate (once more) that W_{sol} does not fall monotonically. In order to interpret fractionation experiments, the authors assumed that W_{sol} reflects Z1 or, in other words, that the difference between W_{sol} and Z1 is negligible. In our opinion, this approximation leads to biased results. In fact, the weight W_{sol} is the sum of two contributions, one deriving from the homopolymer and the other deriving from the DCM-soluble copolymer. The second contribution is extremely difficult to estimate (since the solubility of a copolymer depends strongly on its sequence distribution) but certainly it is not small. In practice, the measurement systematically underestimates Z1, the error grows as time grows and it quickly becomes unacceptably large.

As an alternative, one may use liquid chromatography (LC). In fact, LC can be used to separate complex mixtures. If the crude mixture obtained by reactive blending of two polymers is injected in the apparatus, the volume at which a macromolecule is eluted, Ve, will depend on chain size
and on the molar ratio, $r_A$, associated with the chain ($r_A$ is equal to the ratio $m/s$, where $s$ is the chain size and $m$ are the number of A units in the chain). It has been reported that, for some copolymer systems, conditions can be found in which $V_e$ is independent from the molar mass. The cited systems possess a peculiarity, namely the two repeat units, A and B, possess very different structures. A mixture of PC and Nylon 6 was considered. They are structurally different since PC possesses two aromatic rings (see structure) whereas Nylon 6 is fully aliphatic.

A calculation was performed assuming that LC separates in a size-independent manner. Figure 1 reports the simulated chromatogram for a copolymer, PC–Nylon 6, obtained by melt-mixing. For sake of simplicity, it was assumed that $V_e$ follows a linear law of the type $V_e = g_0 + g_1 r_A$, with $g_0 = 1$ mL and $g_1 = 2$ mL and that the resolving power is almost infinite. As a result, the two homopolymers elute almost exactly at $V_e = 1$ mL and $V_e = 3$ mL, with very small spreads around these values. On the other hand, the peak due to copolymer chains is centered around $V_e = 2$ mL and it is very broad. Actually, it is so broad that it is superposes with Z1 and Z2. This constitutes a small obstacle, that can be easily circumvented by using a deconvolution process to estimate Z1 and Z2. The simulation clearly indicates that LC is expected to be very informative. Experimental studies on LC of melt copolymers are rare. Eersels et al.28 analyzed a copolymer obtained by reactive blending of an aliphatic polyamide, PA46, and an aromatic polyamide, PA6I, by LC. The apparatus can separate a mixture of two homopolymers, indeed (PA46 is eluted at 30 min whereas PA6I is eluted at 70 min). However, the LC trace for the copolymer does not fulfill the expectations. It shows a steep increase at 30 min followed by a monotonic decrease until it reaches a value close to zero at 70 min. The measurement of Z1 and Z2 turns out to be too difficult. However, if one assumes that PA46 elutes between 30 and 33 min (i.e. that the elution behavior of PA46 homochains is not “disturbed ” by the copolymer chains), by taking the ratios, one can estimate the quantity $Z_1/(Z_1+Z_2)$. In summary, much works still needs to be done and the potential of the LC technique has not been tested yet.

Nuclear magnetic resonance (NMR) is widely used to study exchange reactions in polymers5–35 and many authors used NMR spectra to estimate the number of average lengths $<n_A>$, $<n_B>$ and the degree of randomness, $B_{ran}$. However, to the best of our knowledge, the measurement of $Z_1$ and $Z_2$ has never been performed. The reason is not clear. In order to shed some light on this obscure subject, we considered the reactive blending of two polyesters of the type FFFFFFF and DDDDDD where the repeat unit, F, is phenol phtalain terephthalate and D is a dimethyl derivative of bisphenolA terephthalate.

Figure 1. Simulated LC chromatogram of a copolymer obtained by reactive blending of PC and Nylon 6.
Figure 2 reports the simulated NMR spectrum for the copolymer obtained by reactive blending of poly(F) and poly(D). Peaks are resolved up to the tetrad level, similar to the spectrum by Matlengiewicz. The spectrum has 28 peaks and it is dominated by the peaks at 9.08 and 9.75 ppm due to FFFF and DDDD, respectively. Their intensity is the sum of two contributions, Cc and Ch, where Cc is due to FFFF and DDDD sequences which belong to the copolymer and Ch is due to the unreacted homopolymer. In order to estimate Z1 and Z2, one must rule out the peaks at 9.08 and 9.75 ppm, consider the remaining 26 peaks and perform a deconvolution. Fitting the intensities with a sequence distribution model (the first order markoffian one), one obtains Cc and the weight of the unreacted homopolymer is easily obtained using the formula Z1 = Ch–Cc.

As a matter of fact, the cases in which the NMR spectrum displays peaks resolved up to the tetrad level are very rare. The most common case is when the three dyads, AA, AB, BB, are resolved. In this case, to the best of our knowledge, nobody has ever reported that NMR can be used (alone) to estimate Z1 and Z2.

Mass spectrometric methods for measuring the amount of unreacted homopolymer

The MS analysis of melt copolymers has been performed by us and by others. MS is very appealing since, in the MS spectrum, peaks due to homopolymer and copolymer chains are fully separated. Taking the sum of the intensities of the MS peaks due to homopolymer A and B, one finds Z1 and Z2. At a first glance, any MS technique is amenable to perform the analysis. However, this is not the case. In fact, hard-ionization MS techniques may yield a large number of peaks due to dimers and trimers and these small oligomers are not very informative. The reason is best explained with an example. In the MS spectrum of an AB copolymer which is random and equimolar, the dimer intensities ratio A2 / AB / B2 is 25/50/25. Thus, peaks due to homopolymer and copolymer chains are superposed. On the other hand, soft-ionization MS techniques such as MALDI usually yield peaks spanning over a wide mass range and also a few of small oligomers vanish. In the following, two examples will be discussed.

Samples HH10, HH15, HH30, HH60 HH90 HH180 were obtained heating an equimolar mixture of Nylon6,6 (referred to as G) and Nylon6,10 (referred to as H) at 290°C for 10, 15, 30, 60, 90 and 180 minutes, respectively. Before the reaction, the type and the abundance of end-groups was measured: Nylon6,6 chains turned out to be carboxyl-terminated. Figure 3 reports the simulated MALDI spectrum of the sample HH60. It displays peaks due to octamers, nonamers and decamers, up to undecamers, along with assignment. For instance, the peak at mass 1995.6 is due to G8 (the Ny6,6 octamer), whereas the peak at mass 2219.6 is due to H8 (the Ny6,10 octamer). The experimental mass spectrum shows peaks at lower masses, i.e. peaks due to trimers, tetramers, pentamers, up to octamers. The analysis of the MALDI spectra yields an estimate for the weight of unreacted homopolymer Z1 and Z2.

Poly(hydroxybutyrate) (briefly PHB) and PHB-rich copolymers can be obtained by microbial synthesis (mass spectra of these copolymer have been published). However, Adamus et al. believe that this route is not optimal and that chemical synthesis must be preferred. Figure 4 reports the simulated MALDI spectrum for a copolymer obtained by reactive blending of “synthetic” PHB and poly(caprolactone) (briefly PCAPL). It also reports peak assignments (M for PHB repeat unit and C for PCAPL.
repeat unit). All peaks are due to chains terminated by hydroxyl groups which are detected as sodium cations. For instance, the peaks at mass 1296.5, 1384.5 and 1524.5 are due to the PCAPL 11-mer, 12-mer and 13-mer. From the inspection of the figure, it can be seen that theory predicts two peculiar effects, namely that isotopic-peak superposition occurs in a weak manner (actually very weak) and that peak-free regions alternate with regions in which peaks tend to form triangle-shaped clusters. The experimental spectrum confirms the two predictions. Opportune decoding

![Graph](image1.png)

**Figure 3.** Simulated MALDI spectra of two copolymers obtained by reactive blending of Ny6,6-Ny6,10 at 290 °C for 60 min.

![Graph](image2.png)

**Figure 4.** Simulated MALDI spectrum for a copolymer obtained by reactive blending of PHB and poly(caprolactone).
of the information contained in the MALDI spectra of PHB-PCAPL yields an estimate for the weight of unreacted homopolymer Z1 and Z2.

It is quite apparent that the topic of the measurement of Z1 and Z2 is connected with the topic of the bivariate distribution of chain sizes and compositions. As a matter of fact, the bivariate for a sample obtained by reactive blending is composed of three parts, Z1, Z2 and Z3. It is a surface with two strong minima at \( r_2 = 0.999 \) and at \( r_5 = 0.001 \) (\( r_A \) was defined in the LC section). At low masses, Z3 is very strongly superposed with Z1 and Z2. As the mass grows, the width of the compositional distribution decreases quickly and the superposition ceases.

**Conclusion**

MALDI is the method of choice for measuring the amount of unreacted homopolymer during reactive blending.

**References**

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