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# 2D Chromatographic Analysis of Graft Copolymers Obtained by Copolymerization of Macromonomers via Conventional, Controlled Radical, and Anionic Polymerizations

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## Introduction

Graft copolymers offer all properties of block copolymers but are usually easier to synthesize. Moreover, the branched structure offers important possibilities of rheology control. Depending on the nature of their backbone and side chains, graft copolymers can be used for a wide variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers, viscosity index improvers, and polymeric emulsifiers.[1,4]

The state-of-the-art technique to synthesize graft copolymers is the copolymerization of macromonomers (MM) with low molecular weight monomers.[2] In most cases, conventional radical copolymerization has been used for this purpose. Using living polymerizations for both the synthesis of the macromonomers and for the copolymerization offers the highest possible control of the polymer structure.

In all these copolymerizations, beside the desired graft copolymers with at least two side chains, a number of unwanted products can be expected: unreacted macromonomer, ungrafted backbone, and backbone with only one graft ("star copolymer"). The latter is undesirable for applications as thermoplastic elastomer.

Conventional and controlled copolymerizations lead to different copolymer structures. In conventional radical copolymerization the polymers show a broad molecular weight distribution (MWD) and chemical heterogeneity of first order. The chemical composition of different polymer molecules is different due to the short period of time needed to form a polymer and the shift of the comonomer ratio during polymerization. In a living polymerization (e.g., ATRP, anionic polymerization) all chains grow simultaneously with the same chemical composition but this changes during the polymerization leading to a heterogeneity of second order, i.e. a compositional shift within all of the chains, accompanied by a narrow MWD.

In this paper we wish to demonstrate that the combination of two different chromatographic techniques can be used in order to obtain complete information on the structure and composition of graft copolymers. In the first dimension, separation according to chemical composition is performed by Liquid Adsorption Chromatography followed by injection into SEC which provides information on the total MWD. It was shown earlier that this procedure provides important information on the structure of block copolymers.[3] We will show how this principle can be expanded to graft copolymers.

## Experimental

**Synthesis**: Conventional and controlled radical as well as anionic copolymerizations of n-butyl acrylate (nBuA) with PMMA macromonomers (made by group transfer polymerization[4,9]) were used for the synthesis of graft copolymers. In radical copolymerizations the PMMA macromonomer had a methacryloyl head group, in anionic copolymerization an acryloyl headgroup was used. Conventional radical polymerization was initiated by AIBN at 60 °C in butyl acetate as solvent.[4] In ATRP the polymerization was initiated by methyl α-bromopropionate in diphenyl ether at 90 °C in the presence of a mixture of CuBr, copper powder, and 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbipy) as catalyst.[5] In anionic polymerization the reaction was initiated by ethyl α-lithioisobutyrate in the presence of a 2:1 complex of triisobutylaluminum and CsF in toluene at –78 °C.[6]

**Characterization**: The graft copolymers were characterized by 2-dimensional chromatography.[3] An HPLC and a SEC apparatus are connected by a dual-loop automatic injector. The HPLC was used under critical conditions of adsorption (LACCC)[7] for PnBuA: eluent, THF:acetonitrile (53:47 by weight); flow, 0.01 ml/min, 35 °C; column set: 25 cm × 4 mm, RP 18 (YMC S 5 µm), 120 Å and 300 Å (reverse phase). The elute of the HPLC was collected in two sample loops of exactly the same size (100 µl) and was immediately injected onto the SEC. Conditions for SEC: THF as eluent at a flow rate of 2 ml/min, RT, column set: 2 x 30 cm, 5 µm PSS SDVgel, linear and 100 Å. Detectors: TSP UV3000 diode array detector and PL EMD-960 evaporative light scattering detector (ELSD) at 40 °C with a gas flow of 3.5-5 l/min. The PSS 2D SEC software (Polymer Standards Service GmbH, Mainz) was used for collecting and evaluating the raw data.

## Results and Discussion

**1D Methods:** Fig. 1 shows a SEC eluogram of a graft copolymer made by conventional radical copolymerization. A broad peak is observed; the shoulder is due to residual macromonomer. Since only linear PMMA standards were used for calibration, the molecular weight averages are apparent only.

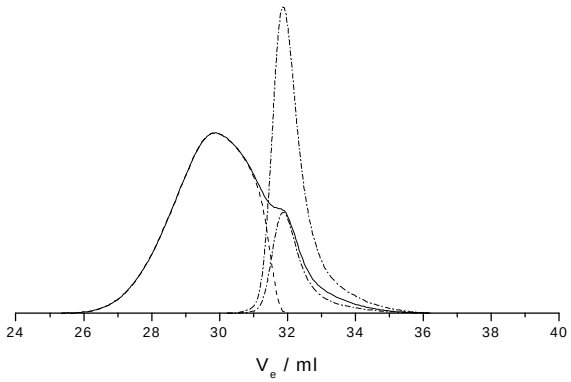


**Figure 1**: SEC trace of a graft copolymer obtained by conventional radical polymerization. Crude product (—), graft copolymer (---, $M_{n,app}$ = 54800, PDI = 1.7), PMMA MM (-·-, $M_n$ = 10900, PDI = 1.19).

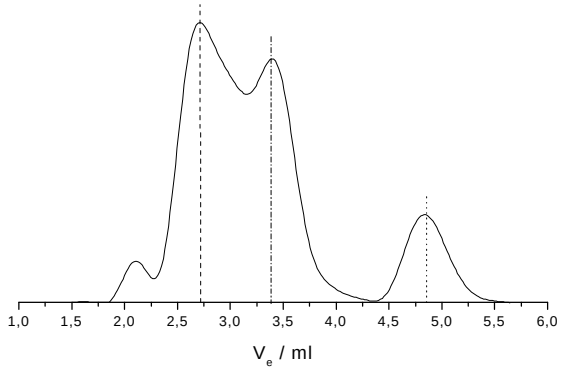


**Figure 2**: LACCC trace of a graft copolymer obtained by conventional radical polymerization. Graft copolymer (---), PMMA MM and star copolymer (-·-), PnBuA homopolymer (···).

In LACCC, conditions were chosen in a way that PnBuA of different molecular weights all elute at the same elution volume (critical point of adsorption). Under these conditions, PMMA elutes in SEC mode and it was shown for block copolymers that separation occurs only according to the molecular weight of the PMMA block.[8] In our case it was assumed that similarly, separation occurs according to the total number of PMMA side chains in a given elution volume. Fig. 2 shows three peaks which were assigned with a series of homopolymers: at 4.7 ml we observe PnBuA homopolymer, i.e. backbone without any grafts, at 3.4 ml residual macromonomers elute, however this peak also may contain graft copolymers with exactly one side chain ("star copolymers") which are expected to elute at the same volume since they contain the same number of PMMA segments. Finally, at 2.7 ml we find a broad peak which corresponds to the graft copolymer. The maximum corresponds to a polymer containing ca. 4 side-chains per backbone, as determined from the PMMA calibration curve.

**2D Chromatography**: Both one-dimensional methods only give a partial view of the true composition of the copolymer. Fig. 3 shows a two-dimensional chromatogram of the same graft copolymer, indicating that four different species are present in the product. Integration of the peaks allows for

quantitative determination of the composition and shows that in conventional radical copolymerization under these conditions we only find 63% of the desired product.

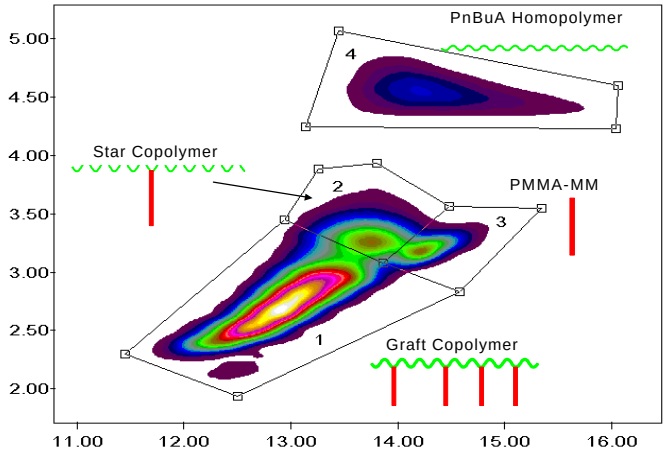


**Figure 3**: 2D chromatogram of PnBuA-*g*-PMMA obtained by conventional radical polymerization. The ordinate corresponds to LACCC elution volume, the abscissa to SEC elution volume. Graft copolymer (1; 63%), star copolymer (2; 17%), PMMA MM (3; 8%), PnBuA homopolymer (4; 9%).

In contrast, ATRP leads to a >90% yield of graft copolymer (Fig. 4). Less than 1% PMMA MM remain in the reaction product, which promises better mechanical properties (as thermoplastic elastomer) of the product. As the chromatogram is scaled linear, the peak of PMMA MM and in the same way star copolymer and PnBuA homopolymer peaks vanish in the signal noise.

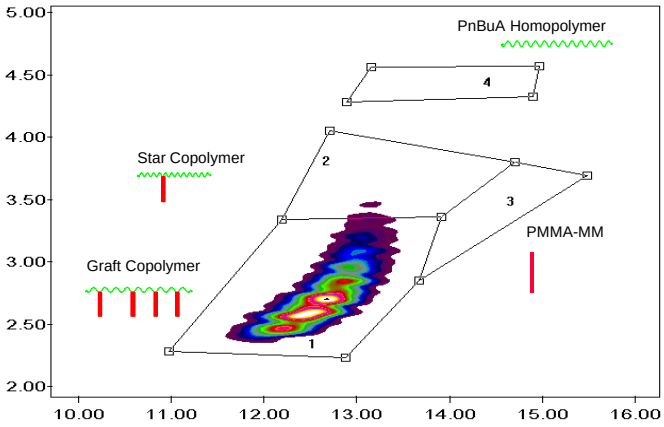


**Figure 4**: 2D chromatogram of a graft copolymer obtained by ATRP. Graft copolymer (1; 91%, $M_{n,app}$ = 72600, PDI = 1.8), star copolymer (2; 6%), PMMA MM (3; 1%, $M_n$ = 5900, PDI = 2.1), PnBuA homopolymer (4; 1%).

In living anionic copolymerization we observe a narrower MWD (Fig. 5), but 31% unreacted PMMA macromonomer is left in the product. Random anionic copolymerization of acrylates and methacrylates is not possible, due to the different nucleophilicities of the anionic chain ends. In the best case a tapered block copolymer would be expected, in the worst case a homopolymerization of the acrylate will occur. Thus, ω-acryloyl-PMMA had to be used as the macromonomer. Since macromonomers usually are less reactive than the corresponding low molecular weight monomers[5,9] it is not unexpected to find considerable amounts of residual macromonomer in the reaction solution. In contrast, ω-methacryloyl-PMMA (which was used in the radical copolymerizations) is four times more reactive.[5]

In addition, a low molecular weight tailing of the graft copolymer peak is observed, containing star copolymer (ca. 18%) and PnBuA homopolymer (ca. 5%). Because of the tailing the quantitative determination of the components by integration is certainly difficult.

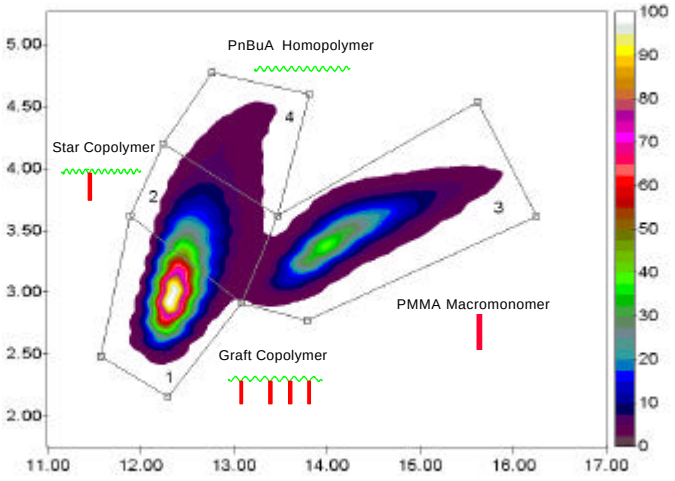


**Figure 5**: 2D chromatogram of PnBuA-*g*-PMMA obtained by anionic polymerization. Graft copolymer (1; 40%, $M_{n,app}$ = 86000, PDI = 1.3), star copolymer (2; 18%), PMMA-macromonomer (3; 17%, $M_n$ = 7800, PDI = 1.8), PnBuA homopolymer (4; 5%).

## Conclusions

2D chromatography presents a useful way to characterize graft copolymers. It is found that the polymers obtained by the three different mechanisms significantly differ in the contribution of the various structures as well as in their molecular weight distribution. Formation of side products can be reduced by using controlled polymerization techniques. The best results are obtained by controlled radical polymerization.

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