

Acrylic Block Copolymer Analysis by Adsorption Chromatography with Evaporative Light Scattering Detection

B. L. NEFF* and H. J. SPINELLI

E. I. du Pont de Nemours and Company, Inc., Marshall Laboratories, Philadelphia, Pennsylvania 19146, and Experimental Station, Wilmington, Delaware 19898

SYNOPSIS

Block copolymers of methyl methacrylate and butyl methacrylate are characterized using silica adsorption chromatography with a toluene-2-butanone solvent gradient. Evaporative light scattering is the detection method for these otherwise hard to detect acrylic polymers. The homopolymer contamination in the diblock materials are well resolved from the diblock in the separation. The major separation mechanism is composition controlled, but the results also indicate a block length dependency on the separation mechanism.

INTRODUCTION

In recent years, a great deal of effort has been aimed at determining the chemical composition distribution (CCD) in addition to the molecular weight distribution (MWD) of copolymers.¹ The CCD introduces a second dimension of architectural complexity beyond the MWD. This can be expressed as a distribution function $H(M, c)$ which has two variables, mass and bulk composition. The CCD can be broken down into greater complexity which is the microstructure of the polymer molecule.² Many of the modern approaches to determine $H(M, c)$ are based on various chromatographic techniques because of the analysis advantage arising from a fractionation. Some of these methods are described in reference 1, and include reverse phase chromatography, adsorption chromatography, precipitation chromatography and cross fractionation.

Block polymers have received considerable attention over the years in both academic studies as well as commercial applications. Diblocks and triblocks are well known to have properties that differ significantly from conventional random copolymers.

They have been used as stabilizers, dispersants, thermoplastic elastomers, and adhesives.

Diblock polymers are often made by a sequential addition of monomers to a living polymer chain. These living polymers can be made by either anionic polymerizations for styrene and various dienes or by group transfer polymerization (GTP) for methacrylates.

Group transfer polymerization is a new type of living polymerization discovered by DuPont³ that can be used to make block polymers. It involves the repeated catalyzed addition of monomer to a growing polymer chain which carries a reactive silyl ketene acetal (Fig. 1). During the addition, the silyl group transfers to the incoming monomer. This generates a new ketene acetal function that is ready for reaction with more monomer. This type of polymerization can be used to control the architecture of polymers. It has been used to make block polymers,⁴ stars,⁵ and macromonomers.⁶

A key characterization of diblock polymers made with any living polymerization process is the level of homopolymer contained with the diblock. The analysis of the level of homopolymer may help in understanding the polymerization processes, termination reactions, and efficiencies. At the very least, the amount of homopolymer present will dilute the properties of the diblock.

* To whom correspondence should be addressed.

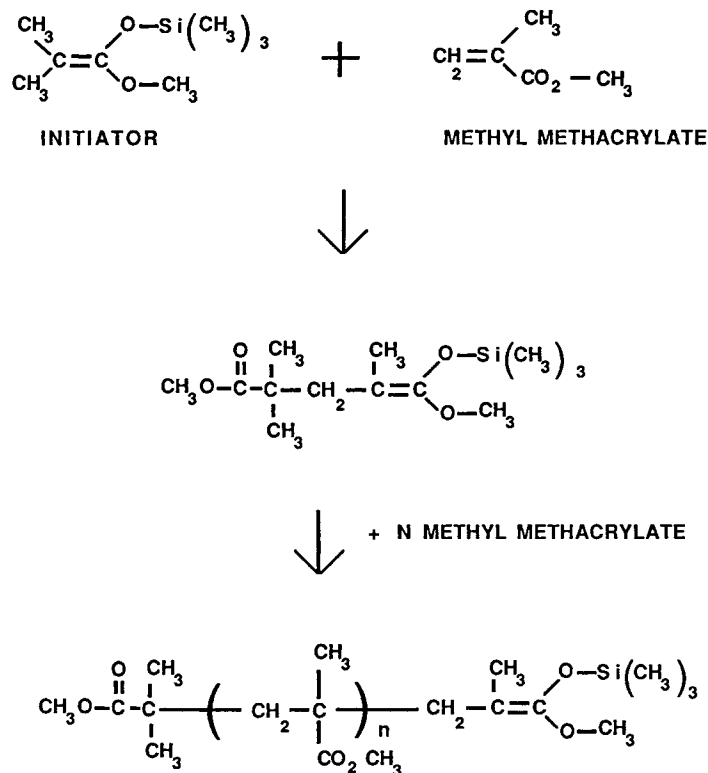


Figure 1 Polymerization of MMA by GTP.

Adsorption chromatography offers an excellent way to measure a number of the characterization parameters for block copolymers. It is limited by several problems which show up in polymer chromatography to a greater extent than the more common small molecule chromatography. These include quantitative detection without a chromophore, a limited number of suitable solvents and the need for gradients in the separation. Mourey⁷ has described an adsorption chromatography technique using an evaporative light-scattering detector which overcomes many of the problems listed above. He described a series of experiments characterizing a variety of acrylic copolymers with statistical distributions.

In this paper we will describe the use of this technique to characterize methacrylic diblock copolymers made using group transfer polymerization techniques (GTP). These materials suffer from all the above experimental difficulties as they have no useful chromophore and the type of solvents needed for these systems are not readily used in normal detection systems. Homopolymer contamination is easily measured and the technique can be extended to measure heterogeneity of the diblock.

EXPERIMENTAL

The following is an example of the synthesis of a BMA//MMA 50//50 block polymer. All of the other polymers were made using identical procedures. The monomer compositions and the ratio of monomer to initiator were adjusted to make the desired polymers. All monomers and solvents were purified by passing them through a column of activated alumina. Initiator and catalysts were prepared according to literature procedures.^{8,9}

A 2-L flask was charged with 550 g toluene, 8.67 g (0.0498 mol) 1-trimethylsiloxy-1-methoxy-2-methylpropene, and 0.2 mL of a 1.0 M solution (in acetonitrile) of tetrabutylammonium *m*-chlorobenzoate. A feed of 257 g (1.81 mol) *n*-butyl methacrylate was added over 30 min. Thirty minutes after the NBMA feed was done, a feed of 257 g (2.57 mol) methyl methacrylate was added over 20 min. Sixty minutes after the MMA feed is done, 8.60 g methanol is added to quench the polymer. This made a NBMA//MMA 50//50 block polymer with a molecular weight of $M_n = 10,600$ (theoretical 10,400), $M_w = 13,300$, and $D = 1.25$.

The chromatograph used is a Hewlett-Packard

1090 system equipped with an autoinjector. Polymer samples were eluted using a toluene/2-butanone gradient changing from 98/2% toluene/2-butanone to 100% 2-butanone in 30 min. The column used was a Merck Hibar II 250 × 4.6 mm column packed with Lichrosorb Si 60 (5 μm diameter). Samples were injected from toluene solution at 25 μL of 1–10 mg/mL concentration. The flow path was modified to accommodate the evaporative detector. The detector is a Mark II evaporative laser light-scattering detector manufactured by Varex corporation (Rockville, MD). The drift tube was set at 100°C and the nebulizer nitrogen gas was 20 psi. The solvents were Merck's Omnisolv chromatography grade.

Peak analysis and quantitation was performed using a Nelson analytical chromatography data software system set up on an HP Model 200 computer. Peak area calibrations for homopolymer impurities were measured using GTP produced homopolymers. Light scattering detectors do not produce linear calibrations in general,¹⁰ so the calibration was set up on a computer based spreadsheet to produce a log-log calculation of concentration vs. peak intensity. This is the usual method used to calibrate this type of detector. Concentrations of homopolymer were determined by subtracting the determined homopolymer weight from the total polymer weight in the sample. Calibrations for the block copolymers were not determined and would require careful preparation of calibration materials with a narrow compositional distributions which provide proper coverage of the copolymer's composition range. This work is outside the scope of this paper.

RESULTS AND DISCUSSION

In the synthesis of AB block polymers by GTP, initiator is first reacted with monomer A. This generates a growing, living polymer chain. After all of monomer A has been consumed, monomer B is then added and reacted onto the A polymer segment to make the AB block polymer.

Any termination of the living chain that occurs during the A block formation would result in the presence of some A homopolymer. That is, any living chain that "dies" during formation of the A block is incapable of adding a B block. This results in the presence of homopolymer A along with the AB block polymer.

Termination in group transfer polymerization can occur from two sources. One is the addition of any

active hydrogen materials (alcohol, acids, water, etc.) that might be present as impurities in either the solvents or the monomers. These materials react with the silyl ketene acetal group on the end of the chain, remove the silicone, and deactivate the chain end [Fig. 2(a)]. The other method of termination is from an internal backbiting reaction¹¹ [Fig. 2(b)]. This reaction can occur throughout the polymerization process and involves the reaction of the living end with an internal ester.

If no termination occurs during the entire polymerization procedure, then only AB polymer will form. If all of the chain ends are terminated during the A block formation, then no polymerization of the B monomer will occur and only homopolymer A will be formed. If some of the chain ends are terminated during the A block formation step, the a mixture of A and AB polymer will form. The ratio of the two will give an indication of the amount of termination that occurred. There is no way for homopolymer B to form either by itself or in combination with AB block during these polymerizations. Homopolymer of B can form only if the B monomer is polymerized first.

The samples studied in this work are GTP synthesized block polymers consisting of a methyl methacrylate segment and a butylmethacrylate segment. The material is synthesized by first producing a living pBMA fragment and adding MMA monomer after the BMA is reacted, to obtain the block architecture. Figure 3 shows a HPLC chromatogram of one such polymer. This polymer has a nominal molecular weight of 10 K g/mol (as measured by GPC using a PMMA calibration) with a 1/1 mole ratio of monomers. The first peak is the pBMA homopolymer contaminate and the second peak is the block polymer. The pBMA retention time was verified with independently synthesized homopolymer as was pMMA, which elutes after the diblock polymer. This agrees with the theoretical prediction that retention time increases with decreasing pendant chain length¹² (butyl to methyl) and with the results for random polymers presented by Mourey (Ref. 4). We do not expect any pMMA homopolymer contamination because the only initiator in the living system at the time of MMA addition is the pBMA fragment. The homopolymer contaminate is caused by the various chain termination mechanisms listed in the synthesis description.

This chromatogram illustrates how readily homopolymer content and block heterogeneity is obtained with this method. Because of the baseline resolution between the block and the homopolymer,

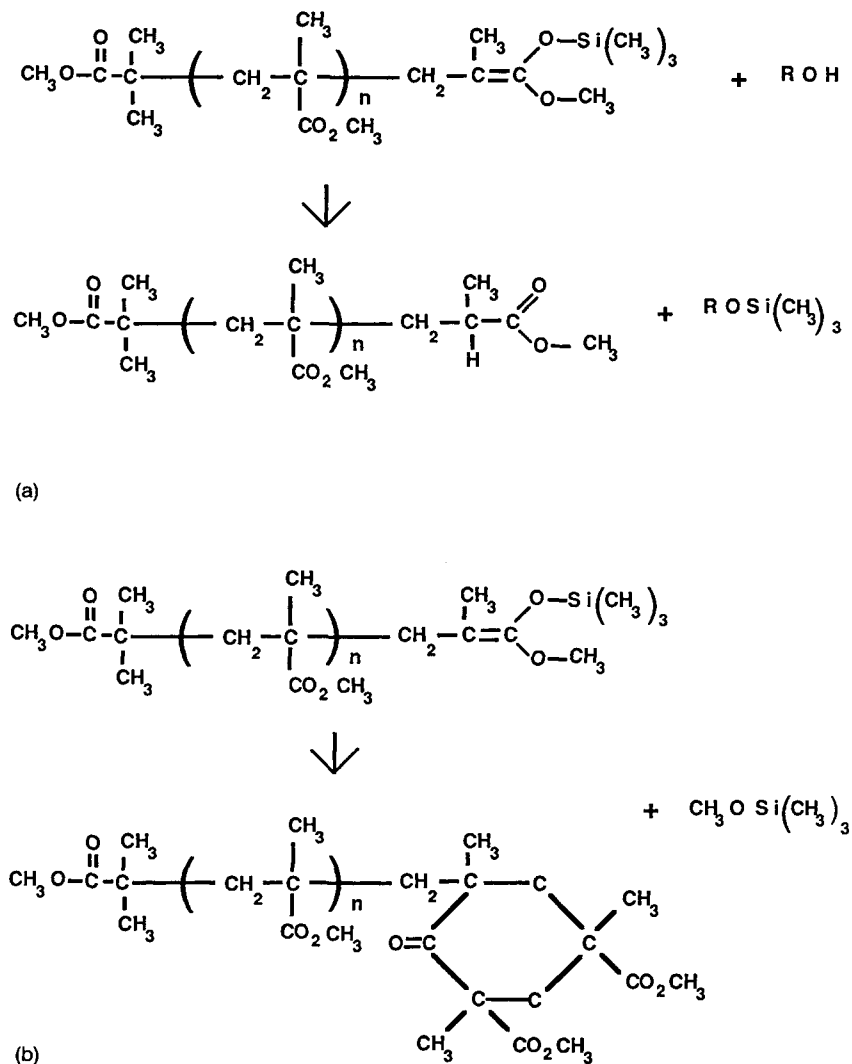


Figure 2 (a) Termination by alcohol; (b) termination by internal backbiting.

the concentration of homopolymer is easily determined. For this system, we measured a three percent by weight contamination. By visual examination, the level seems higher but as pointed out earlier the calibration response for light scattering detection is not linear. The scattering intensity depends on the refractive index of the polymer and the droplet size and distribution produced in the nebulizer of the evaporative detector¹³ which is further complicated by the fact the detection temperature is between the glass transition temperature of the two components of the diblock. The next feature to note is the breadth of the diblock peak. This technique fractionates polymers based on composition with very little molecular weight dependence. The narrow breadth seen in the homopolymer is an illustration of its compositional purity. Diblock polymers made

by the GTP process (living polymer) have a distribution of composition which is broader than the statistical equivalent.¹⁴ This is illustrated in Figure 4 which is a chromatogram of a random MMA/BMA (1/1 mole ratio) copolymer made by the GTP process. The width of this peak is substantially less than the peak in Figure 3. The wide variation in peak widths indicate the heterogeneity comparisons could be described by a rigorous statistical technique such as determining composition moments of the distribution. A description of this is not within the scope of this article.

The retention behavior of random copolymers shows a smooth variation as a function of composition.¹⁵ Copolymers have retention times intermediate to those of the homopolymers. This is also true of the block systems we studied. However, the re-

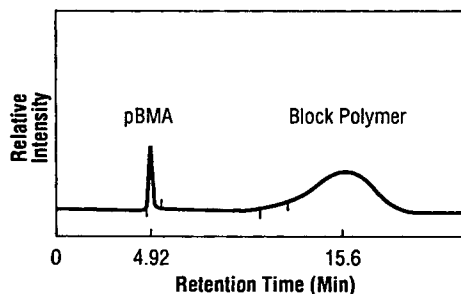


Figure 3 MMA/NBMA (1/1 mole ratio) block polymer with $M_n = 10$ K g/mol synthesized using GTP process. Notice baseline resolution between homopolymer and block copolymer. Homopolymer contamination of 3%.

Retention times of intermediate compositions are also influenced by block length, an effect not immediately apparent in random systems. A first indication of this is seen in Figures 3 and 4 as the block system with a similar bulk composition to the random polymer has a retention time much closer to the homopolymer PMMA retention time (~ 20 min in this case).

This effect is readily seen in a series of materials we synthesized to illustrate the variation of retention time with block architecture. Figure 5 shows the change in the peak maximum for two diblocks (samples A and B) of similar M_n compared to a polymer with the same bulk composition as sample B but with an M_n four times greater. The increased PMMA content in the 10 K block shifts the peak maximum toward the homopolymer PMMA retention time as expected. However, when the bulk composition is kept constant and the block lengths increased, as in the high M_n diblock polymer, the peak maximum shifts further to the PMMA peak position.

This can be explained by considering how the retention factor for each repeat unit is averaged for

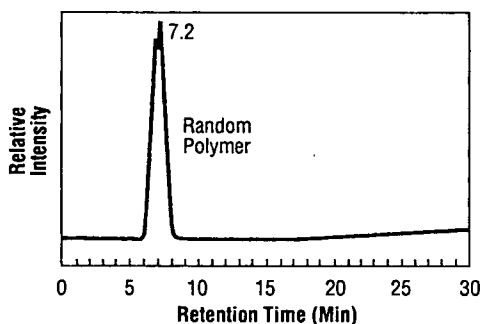


Figure 4 Random copolymer of MMA/NBMA (1/1 mole ratio) with $M_n = 10$ K g/mol synthesized using GTP process.

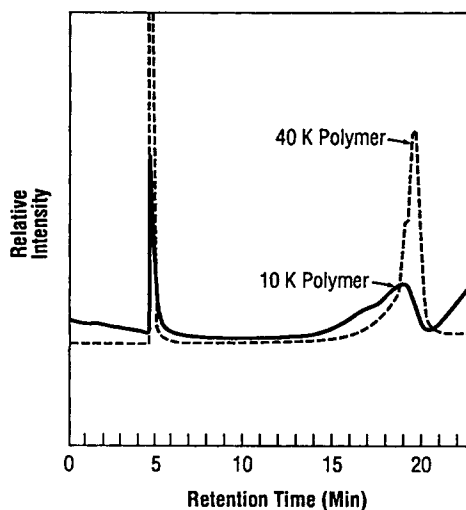


Figure 5 Comparison of two diblocks of MMA/NBMA (1/1 mole ratio) with equivalent bulk compositions and different M_n 's 10 K and 40 K. These samples have homopolymer contamination levels of 10%.

block polymers and random copolymers. In a random system the probability of finding a long chain of PMMA is highly improbable, however it is the norm in the block materials and explains why the peak position for the block is closer to PMMA than the random composition equivalent.

In a second set of experiments we varied the BMA block length while maintaining a constant MMA block. The chromatograms are shown in Figure 6 and the compositions are listed in Table I. We can see the effect of increasing BMA producing a reten-

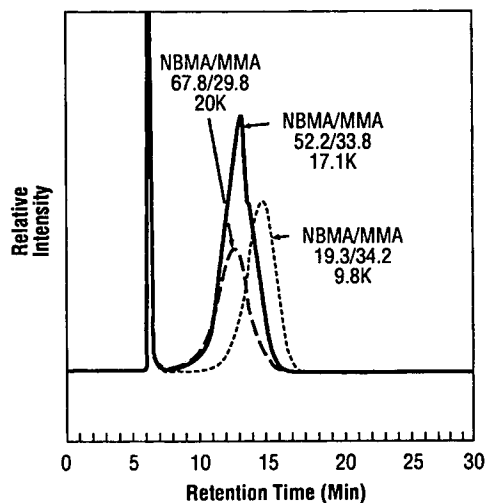


Figure 6 Comparison of three diblocks of MMA/NBMA with constant a MMA length and varying NBMA lengths.

Table I

Sample	Composition (NBMA/MMA mol)	M_n (g/mol)
A	19.3/34.2	9.8K
B	52.2/33.8	17.1K
C	67.8/29.8	20K

tion time closer to the pBMA peak maximum. The change in retention time is smaller for these samples than that for the first set even with the very large change in bulk composition. Because of its greater affinity of PMMA for the Si column, the PMMA block length is the major controlling factor in determining retention times under these conditions.

The results of these experiments varying block length indicates this technique could be used to characterize block length distributions in addition to homopolymer contamination and bulk composition. In the extreme case of block systems, bulk composition plays a minor role compared to the relative block length of the most strongly absorbing monomer unit. There are many systems which have non-random distributions of comonomers which are not as extreme as the diblock materials we used. The large sensitivity of the normal phase absorption experiment to block length indicates this method has great promise for block length distribution characterization. One difficulty would be obtaining appropriate calibration samples. This was not a problem with our GTP acrylic polymers. The structural control that GTP allows gives the ability to synthesize a variety of calibration polymers.

The examples shown here are acrylic polymers synthesized using group transfer polymerization techniques. The chromatography conditions used are the ones described by Mourey¹⁶; however, there is no reason stay with these conditions. We have used methylene chloride as the carrier solvent, which is an excellent acrylic solvent (toluene is not a universal acrylic polymer solvent) and is more readily

evaporated in the detector than toluene. Whatever the gradient configuration, the above examples illustrate the capability of this method to detect homopolymer contamination in block polymers and the strong dependence on block length on the separation mechanism.

REFERENCES

1. G. Glockner, in *Advances in Polymer Science* 79, Springer-Verlag, New York, 1986.
2. J. L. Koenig, "Chemical Microstructure of Polymer Chains," Wiley, New York, 1980.
3. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B., Farnham, and T. V. RajanBabu, *J. Am. Chem. Soc.*, **105**, 5709 (1983); D. Y. Sogah and O. W. Webster, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 927 (1983); D. Y. Sogah, W. R. Hertler, O. W. Webster, and G. W. Cohen, *Macromolecules*, **20**, 1473 (1987).
4. C. S. Hutchins and A. C. Shor, U.S. Pat. 4,656,226 (1987); J. A. Simms and H. J. Spinelli, *J. Coat. Technol.*, **59**(742), 125 (1987).
5. H. J. Spinelli, U.S. Pats. 4,659,782 and 4,659,483 (1987); *Int. Conf. Org. Coatings Sci. Technol.*, **13**, 417 (1987).
6. H. J. Spinelli, *Int. Conf. Org. Coatings Sci. Technol.*, **14**, 333 (1988); J. A. Simms and H. J. Spinelli, *ibid.*
7. T. H. Mourey, *J. Chromatogr.*, **357**, 101 (1986).
8. A. Revis, U.S. Pat. 4,746,750 (1988).
9. I. B. Dicker, et al. U.S. Pat. 4,588,795 (1986).
10. L. E. Oppenheimer and T. H. Mourey, *J. Chromatogr.*, **323**, 297 (1985); Varex Corporation operating manual.
11. W. J. Britain and I. B. Dicker, *Macromolecules*, to appear.
12. L. R. Snyder, *Principles of Adsorption Chromatography*, Dekker, New York, 1968.
13. T. H. Mourey and L. E. Oppenheimer, *Anal. Chem.*, **56**, 2427 (1984).
14. J. Stejskal and P. Kratochvil, *Makromol. Chem.*, **188**, 2435 (1987).
15. G. Glockner, in *Advances in Polymer Science* 79, Springer-Verlag, New York, 1986.
16. T. H. Mourey, in Ref. 15.

Accepted March 6, 1990