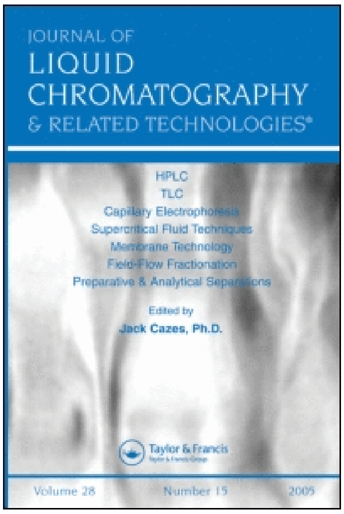

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Armstrong, Daniel W. , Bui, Khanh H. and Boehm, Richard E.(1983) 'Practice, Mechanism and Theory of Reversed Phase TLC Polymer Fractionation', Journal of Liquid Chromatography & Related Technologies, 6: 1, 1 — 22
To link to this Article: DOI: 10.1080/01483918308066866
URL: http://dx.doi.org/10.1080/01483918308066866

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(1), 1-22 (1983)

PRACTICE, MECHANISM AND THEORY OF REVERSED PHASE TLC POLYMER FRACTIONATION

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ABSTRACT

The use of reversed phase TLC to determine the molecular weight and molecular weight distribution of poly(methyl methacrylate), poly(ethylene glycol), poly(ethylene oxide), poly(tetrahydrofuran), poly(butadiene), poly(isoprene), poly(α-methylstyrene) and poly(styrene) is demonstrated. The mechanism by which fractionation occurs and a theoretical description of the process are given and discussed.

INTRODUCTION

Among the more basic and important analytical problems in polymer chemistry is the determination of molecular weights. There are a variety of primary techniques (i.e., those which theoretically do not require molecular weight standards; such as light scattering, osmometry, ebulliometry, cryoscopy, sedimentation, small angle X-ray scattering, etc.) and secondary techniques (i.e., those which require molecular weight standards, such as viscosity and gel permeation chromatography) available for these measurements. Because of its flexibility and efficiency, gel permeation chromatography (GPC) has become one of the more

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widely used techniques in polymer analysis. Recently it was reported that poly(styrene) could be fractionated more efficiently (than with GPC) using conventional reversed phase TLC and/or LC (1). This fractionation was the result of selective precipitation or dissolution of these polymers. In reversed phase TLC a binary solvent mobile phase was found to change naturally in composition during development because of selective adsorption of the more nonpolar solvent by the stationary phase. The changing composition of the mobile phase, during development, could cause polymer fractionation if the more adsorbed component of the mobile phase was a thermodynamically "good" solvent while the less adsorbed component was a thermodynamically "poor" solvent.

In the present work, this technique is extended to several more polymers. Further evidence is given for the precipitation mechanism of separation. Finally, a recently developed theory for the observed chromatographic behavior of poly(styrene) (2) is explained in general terms as it applies to the reversed phase TLC fractionation of homopolymers.

MATERIALS

Whatman KC18F reversed phase TLC plates (5 x 10 cm, 5 x 20 cm and 20 x 20 cm) were used in the TLC fractionation of poly(styrene), poly(α-methylstyrene), poly(isoprene), poly(butadiene), poly(methyl methacrylate), poly(ethylene glycol), poly(ethylene oxide) and poly(tetrahydrofuran). HPLC grade methanol, methylene chloride, tetrahydrofuran, dioxan (from

Baker Chemical Co.) and ethylene glycol (from Sigma) were used as received. The following polymer standards were used: (1) poly (styrene) from Waters Associates, mol wt = 2350, mol wt = 17 500 (Mw/Mn = 1.04), mol wt = 35 000 (Mw/Mn = 1.04), mol wt = 110 000 (Mw/Mn = 1.10), mol wt = 390 000 (Mw/Mn = 1.04), mol wt = 3 700 000 (Mw/Mn = 1.20), mol wt = 10 000 000 (Mw/Mn = 1.30). (2) poly(α-methylstyrene) from Polymer Laboratories, mol wt = 19 500 (Mw/Mn = 1.15), mol wt = 87 000 (Mw/Mn = 1.10), mol wt = 760 000 (Mw/Mn = 1.10). (3) poly(isoprene) from Polymer Laboratories, mol wt = 1360 (Mw/Mn = 1.11), mol wt = 3080 (Mw/Mn = 1.08), mol wt = 12 900 (Mw/Mn = 1.08), mol wt = 33 300 (Mw/Mn = 1.05), mol wt = 113 800 (Mw/Mn = 1.05), mol wt = 260 000 (Mw/Mn = 1.07). (4) poly(butadiene) from Polysciences, mol wt = 500 (Mw/Mn = 1.15), mol wt = 1000 (Mw/Mn = 1.2), mol wt = 3000 (Mw/Mn = 1.2), from Phillips Petroleum Company, mol wt = 90 000 (Mw/Mn = 2.7). (5) poly(methyl methacrylate) from Polymer Laboratories, mol wt = 12 000 (Mw/Mn = 1.1), mol wt = 45 200 (Mw/Mn = 1.09), mol wt = 72 000 (Mw/Mn = 1.08), mol wt = 280 000 (Mw/Mn = 1.15), mol wt = 480 000 (Mw/Mn = 1.16), mol wt = 640 000 (Mw/Mn = 1.16). (6) poly(ethylene glycol) from Polymer Laboratories, mol wt = 106, mol wt = 200 (Mw/Mn = 1.09, mol wt = 415 (Mw/Mn = 1.10), mol wt = 630 (Mw/Mn = 1.06), mol wt = 998 (Mw/Mn = 1/06, mol wt = 1580 (Mw/Mn = 1.06), mol wt = 4820 (Mw/Mn = 1.04), mol wt = 9200 (Mw/Mn = 1.08, mol wt = 11 250 (Mw/Mn = 1.07), ml wt = 19 100 (Mw/Mn = 1.09). (7) poly (ethylene oxide) from Polymer Laboratories, mol wt = 25 000 (Mw/Mn = 1.14), mol wt = 40 000 (Mw/Mn = 1.03), mol wt = 73 000 (Mw/Mn =

1.02), mol wt = 150 000 (Mw/Mn = 1.04), mol wt = 280 000 (Mw/Mn = 1.05), mol wt = 660 000 (Mw/Mn = 1.10), mol wt 1 200 000 (Mw/Mn = 1.12). (8) poly (tetrahydrofuran) from Polysciences, mol wt = 2250 (Mw/Mn = 1.10), mol wt = 7600 (Mw/Mn = 1.07), mol wt = 500 000 (Mw/Mn = 1.18).

METHODS

TLC separations were done in an 11 3/4 in long, 4 in. wide and 10 3/4 in. high Chromaflex developing chamber. The reversed phase plates were not previously equilibrated with the solvent vapor or specially treated in any way. Methylene chloride-methanol was the optimum solvent pair in the TLC fractionation of poly(styrene), poly(α-methylstyrene), poly(isoprene) and poly(butadiene). Dioxan-ethylene glycol was the optimum solvent pair for poly(ethylene glycol) and poly(ethylene oxide) although methanol-ethylene glycol could be used for lower molecular weight polymers (<25000) as well. Tetrahydrofuran-ethylene glycol was the optimum solvent pair for poly(methyl methacrylate) and poly(tetrahydrofuran).

Table I gives the experimental parameters for fractionation of all polymers. It should be noted that the fractionation behavior of all polymers is very sensitive to the composition of the mobile phase in the reservoir (1). The solvent ratios given in Table I are for the fractionation of the greatest range of polymer molecular weights. To examine a specific molecular weight range, one simply alters the volume ratio of the mobile phase (in

TABLE I. Polymers that can be fractionated by reversed phase TLC

Polymer	Solvent Pair	Volume Ratio[c]	Molecular Weight Range[d]	Visualization Method[e]	Development Time	Reference
poly(styrene)	$MeCl_2$:MeOH	(78:22)	10^2 to $5x10^7$	fluorescence quench. or I_2 vapor	f	1
poly(α-methylstyrene)	$MeCl_2$:MeOH	(81:19)	10^2 to 10^7	fluorescence quench. or I_2 vapor	f	this work
poly(isoprene)	$MeCl_2$:MeOH	(82:18)	10^2 to 10^6	spray with 1% I_2 in methanol and let yellow background fade	g	this work
poly(butadiene)	$MeCl_2MeOH$	(80:20)	10^2 to 10^6	1% I_2 spray as above	g	this work
poly(ethylene glycol)	Dioxan:EG[a]	(60:40)	10^2 to 10^6	I_2 vapor	h	this work
poly(ethylene oxide)	Dioxan:EG[a]	(60:40)	10^2 to $1.2x10^6$	I_2 vapor	h	this work
poly(tetrahydrofuran)	THF[b]:EG[a]	(85:15)	10^2 to $5x10^5$	I_2 vapor	h	this work
poly(methyl methacrylate)	THF[b]:EG[a]	(75:25)	10^2 to 10^6	1% I_2 spray as above	h	this work

a) EG=ethylene glycol b) THF=tetrahydrofuran c) The given volume ratio covers the widest range of molecular weights. One can examine a more narrow range of molecular weights (with greater resolution) by altering this ratio slightly. By increasing the initial concentration of the "poor" solvent one fractionates only lower molecular weight polymers. By increasing the initial concentration of the "good" solvent one fractionates only higher molecular weight polymers. (see Experimental Section). d) In most cases the higher molecular weight should not be taken as an absolute limit. Fractionation of higher molecular weight polymers may possibly occur, unfortunately, higher molecular weight standards were not available at the time of this study. e) When using one of the I_2 visualization methods, be sure to remove all traces of the mobile phase from the developed plate (by evaporation or heating in the case of the less volatile solvents) before visualization. f) Closed tank development time = 8 min (5x10 cm plate), 25-40 min (20x20 cm plate). Open tank development times are somewhat longer and dependent on the degree to which the chamber is open. Also, in open chamber development one should start with a 1 to 3% excess of the more volatile solvent. g) Closed tank development time = 8 min (5x10 cm plate), 25-40 min (20x20 cm plate). h) Closed tank development time = 35 min (5x10 cm plate), 3-5 hr (20x20 cm plate).

the developing chamber) by a few percent. For example, if one is interested in fractionating poly(styrene) only in the molecular weight range of 10^2 to 10^4 one would use a mobile phase of 70:30 (v:v) methylene chloride to methanol. This technique also results in increased resolution since one has separated a smaller range of polymers over the same length plate.

All polymer standards were dissolved in the "good solvent" (~5 mg/mℓ) and 1μℓ of this solution was spotted on the TLC plate. The "good" solvent is the first listed of any given solvent pair (e.g., methylene chloride for poly(isoprene), dioxan for poly(ethylene oxide) or tetrahydrofuran for poly(methyl methacrylate)). Developed spots were detected by fluorescence quenching, I_2 vapor or spraying a solution of I_2 in methanol (see Table I). In a few cases tailing of spots occurred near the origin (in closed systems). This problem was eliminated by fractionating the polymers in a partially open system (1). If one spots too high a concentration of the standard, streaking can occur upon development (e.g., for poly(isoprene)). This problem is easily avoided by further dilution of the standards.

RESULTS AND DISCUSSION

For any given polymer there is generally an appreciable number of "good-poor" solvent pairs. Unfortunately, most of the solvent pairs are not effective in the reversed phase TLC fractionation of the polymers. Of critical importance are the relative interactions of the solvents with the stationary phase and the natural gradient that is produced. For TLC fractionation to occur, the stationary phase must preferentially interact with the good solvent thereby enriching the mobile phase in the poor solvent during development. Ideally, the polymer does not substantially interact with the stationary phase until the mobile phase reaches a composition which causes precipitation.

Figure 1 illustrates typical fractionations of poly(isoprene), poly(methyl methacrylate), poly(ethylene glycol/oxide) and poly(butadiene). Table 1 lists all polymers that can be fractionated using this technique at the present time. After testing hundreds of possible mobile phases a few trends have become apparent. Methylene chloride-methanol appears to be the optimum solvent pair for the TLC fractionation of linear unsaturated hydrocarbon polymers (i.e., poly(styrene), poly(α-methylstyrene), poly(isoprene) and poly(butadiene)). For polymers which methanol is a good solvent (poly(ethylene oxide) for example) ethylene glycol seems to be the preferred poor solvent. While ethylene glycol-containing mobile phases generally give good separations and spot shapes, development is somewhat slower due to the increased mobile phase viscosity. Increased resolution often can be obtained by using vapor unsaturated developing chambers provided the good solvent (in the binary mobile phase) is more volatile than the poor solvent (1). The increase in resolution is due to formation of smaller spots and the elimination of tailing near the origin. A possible mechanism by which this is accomplished can be envisioned. The binary mobile phase (in the

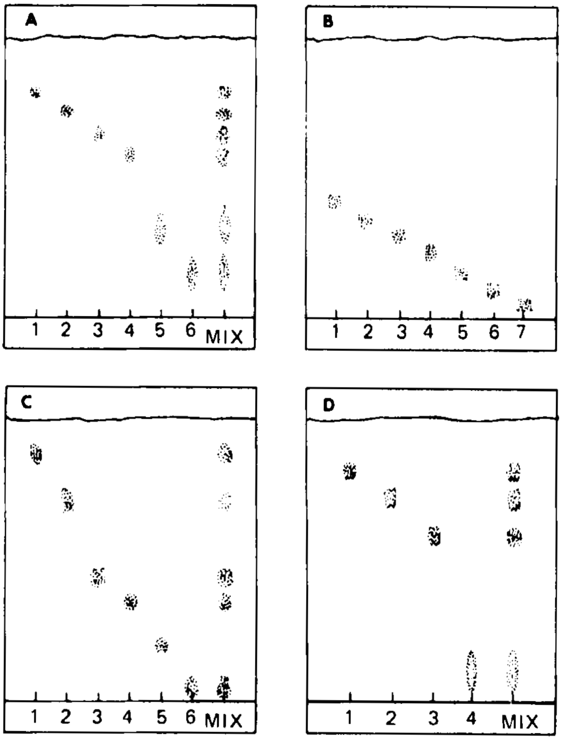

Figure 1: Schematic illustrating typical reversed phase TLC fractionations of:

(A) poly(isoprene) with 81:19 (v:v) methylene chloride:methanol.

1 = $1.36\mathrm{x}\ 10^3$; 2 = $3.08\mathrm{x}10^3$; 3 = $1.29\mathrm{x}10^4$;
4 = $3.33\mathrm{x}10^4$; 5 = $1.14\mathrm{x}10^5$; 6 = $2.60\mathrm{x}10^5$

(B) poly(methylmethacrylate) with 74:26 (v:v) tetrahydrofuran:ethylene glycol.

1 = $1.2\mathrm{x}10^4$; 2 = $4.5\mathrm{x}10^4$; 3 = $7.2\mathrm{x}10^4$;
4 = $7.6\mathrm{x}10^4$; 5 = $2.8\mathrm{x}10^5$; 6 =$4.8\mathrm{x}10^5$; 7 = $6.4\mathrm{x}10^5$.

(C) poly(ethylene glycol/oxide) with 57:43 (v:v) dioxyan:ethylene glycol.

1 = $4.15\mathrm{x}10^2$; 2 = $9.98\mathrm{x}10^2$; 3 = $4.8\mathrm{x}10^3$;
4 = $9.20\mathrm{x}10^3$; 5 = $2.5\mathrm{x}10^4$; 6 = $2.8\mathrm{x}10^5$.

(D) poly(butadiene) with 79:21 (v:v) methylene chloride:methanol.

1 = $5\mathrm{x}10^2$; 2 = $1\mathrm{x}10^3$; 3 = $3\mathrm{x}10^3$; 4 = $9.0\mathrm{x}10^4$.

reservoir of the developing tank) acts as a good solvent. However, as it travels up the reversed phase plate it becomes progressively poorer (due to the selective adsorption of the good solvent). Concurrently, the good solvent evaporates at a greater rate than the poor solvent. As a result the gradient tends to be accentuated, precipitation occurs sooner and R_f values are lower. Because of the gradient, the leading edge of a precipitated spot is in contact with a slightly poorer solvent than the trailing edge. When development continues after precipitation, the mobile phase moving past the spot becomes a somewhat better solvent. This results in a relatively slow movement of the spot with the trailing edge being affected more than the leading edge. This mechanism also explains the somewhat unusual (square or rectangular) spot shapes that often accompany this separation technique.

The R_f of all reported polymers tends to vary with the log of their molecular weight (see Figures 2 and 3). For the highest molecular weight polymers, the relationship becomes nonlinear and the resolution is not as good (Figure 2). The R_f-log molecular weight relationship holds for vapor unsaturated development as well (Figure 3). The slope of the calibration curve varies with the degree of evaporation allowed. Since standards and unknowns are generally run on the same plate this poses no inconvenience.

In all cases the separation of polymers is assumed to be due to a precipitation mechanism. This is somewhat unusual as most chromatographic separations result from adsorption or partition

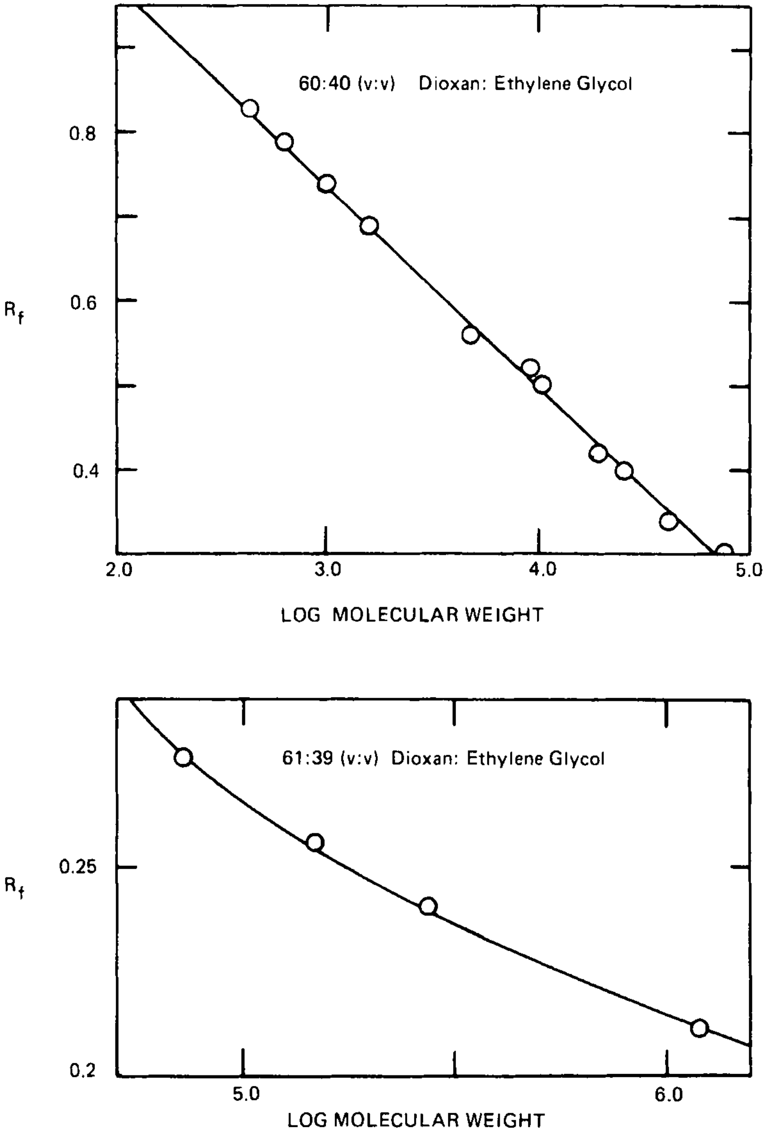

Figure 2: Plot of R_f versus log molecular weight for poly(ethylene glycol/oxide). Note that the relationship is linear up to a molecular weight of ~10^5.

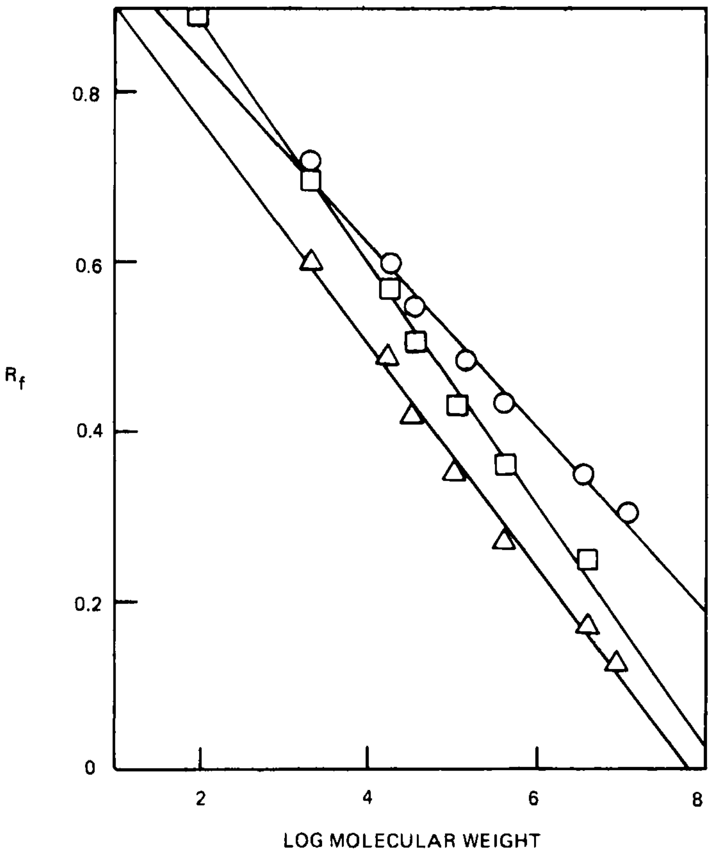

Figure 3: Linear calibration curves for poly(styrene) standards developed in vapor unsaturated Chromaflex chamber.

□ = 1/2 in, open lid, mobile phase = 80:20 (v:v) $MeCl_2$:OH

○ = 1 in, open lid, mobile phase = 80:20 (v:v) $MeCl_2$:MeOH

△ = no lid, mobile phase = 80:20 (v:v) $MeCl_2$:MeOH

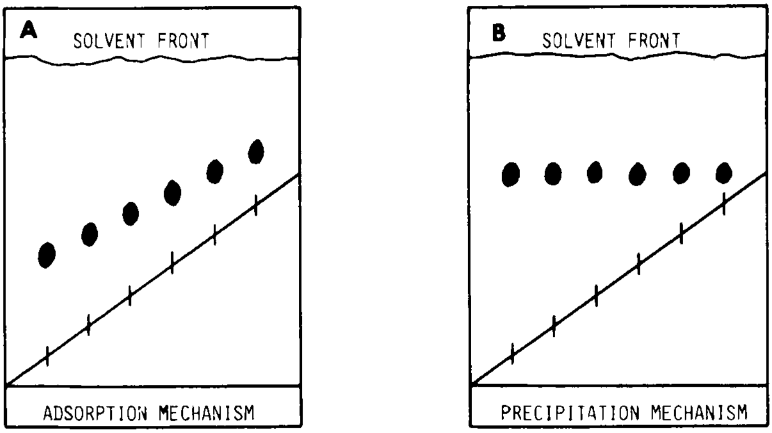

Figure 4: Schematic illustrating the different TLC development patterns expected when a compound's migration behavior is controlled by (A) adsorption processes or (B) precipitation. In both examples a compound is spotted along a line drawn at an angle to the bottom of the plate. The compound in chromatogram A has an R_f of 0.33. The compound in chromatogram B tends to travel with the solvent front until some process (e.g., change in mobile phase composition, phase ratio, etc.) causes precipitation.

processes. In ideal situations, the mechanism of separation can be identified with a simple chromatographic test. By spotting a compound diagonally on a TLC plate instead of along a line parallel to the bottom edge, one produces a characteristic development pattern (see Figure 4). Figure 4A illustrates the expected adsorptive chromatographic behavior of a compound (R_f = 0.33) under ideal conditions. In the unusual case where separation is controlled completely by precipitation, one would expect a development pattern as illustrated in Figure 4B (i.e., all spots parallel to the solvent front regardless of "spotting" angle). In reality, one rarely finds perfect examples of either behavior. In the more common case of adsorption TLC, changes in solvent composition (of binary and higher order mobile phases) and phase ratio during development can cause deviations from the theoretical behavior illustrated in Figure 4A. Previous results (1) indicated that the reversed phase TLC fractionation of polymers might exhibit rarely seen behavior characteristic of the precipitation mechanism (Figure 4B). Figure 5 illustrates these results for poly(styrene), poly(isoprene), poly(methyl methacrylate) and poly(ethylene glycol/oxide). At least two molecular weight standards are shown in each case (three in the poly(styrene) example). It is apparent that a polymer of a given molecular weight travels along the developing plate until the mobile phase reaches the critical composition where precipitation occurs. If a polymer is spotted on a TLC plate at a point higher than where the critical composition occurs, it will not move from the origin (note the higher molecular weight polymers in Figure 5).

By plotting the initial volume percent of good and poor solvents in the mobile phase versus polymer R_f value, one can visualize the effect of solvent composition on polymers of different molecular weights (see Figure 6). Each polymer has a characteristic sigmoidal curve. The curve lies closer to the ordinate for higher molecular weight polymers and the variation in solvent composition needed to change the R_f from 1.0 to 0 becomes more narrow with increasing molecular weight. The separation between any two molecular weight curves for the same polymer is indi-

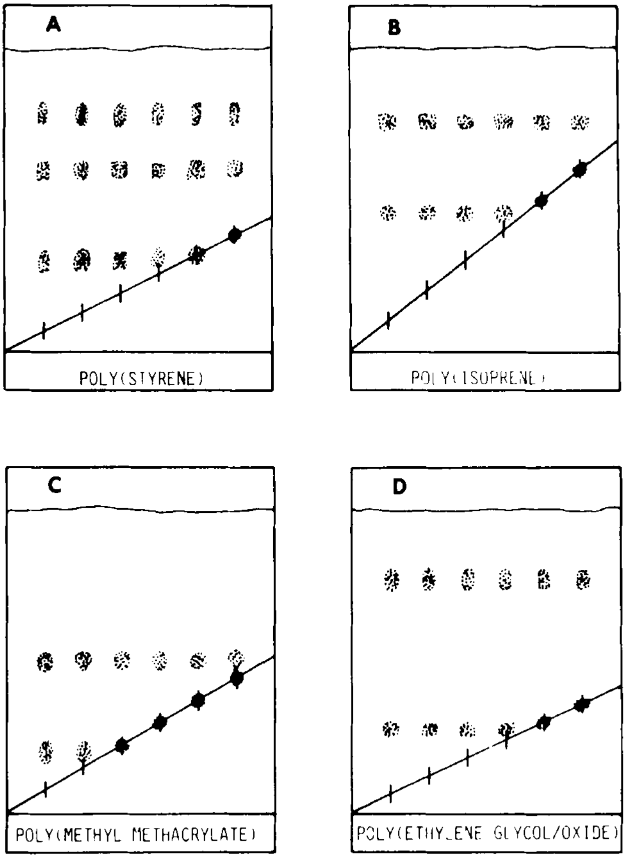

Figure 5: TLC development patterns indicating a precipitation mechanism in the reversed phase fractionation of:

(A) poly(styrene) with 79:21 (v:v) $MeCl_2$:MeOH
(top) MW = 2.35×10^3 (middle) MW = 3.5×10^4
(bottom) MW = 2.7×10^6

(B) poly(isoprene) with 77:23 (v:v) $MeCl_2$:MeOH
(top) MW = 1.36×10^3 (bottom) MW = 3.33×10^4

(C) poly(methylmethacrylate) with 76:24 (v:v) THF:ethylene glycol.
(top) MW = 4.5×10^5 (bottom) MW = 6.4×10^5

(D) poly(ethylene glycol/oxide) with 59:41 (v:v) dioxan:ethylene glycol.
(top) MW = 9.93×10^2 (bottom) MW = 2.5×10^4

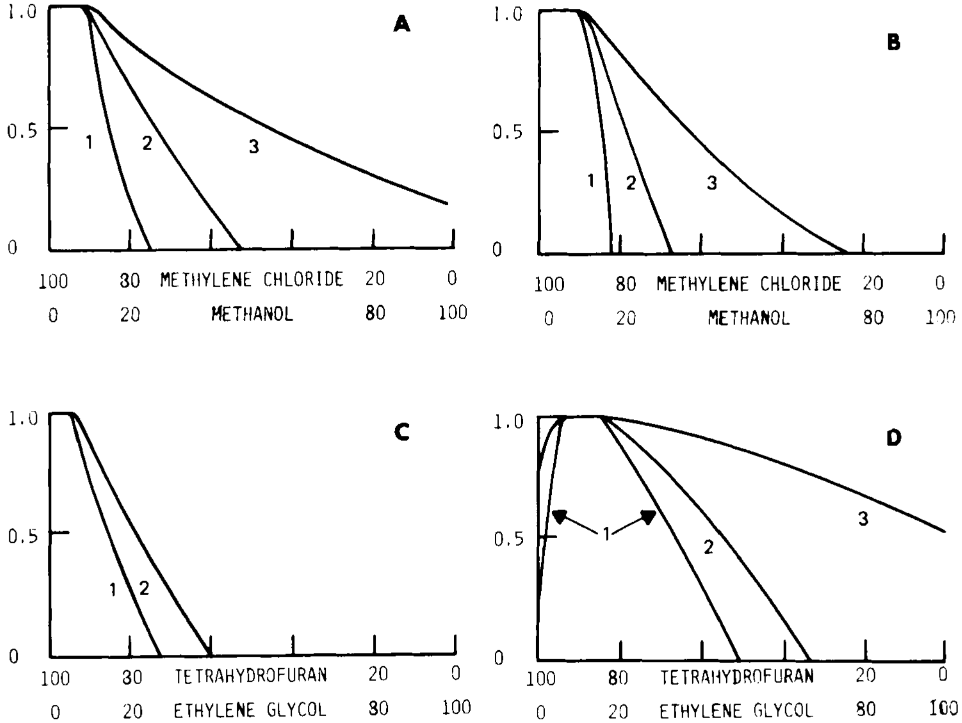

Figure 6: Plots of R_f versus mobile phase composition (volume %). Molecular weights are:

(A) 1 = 9.3×10^4; 2 = 3.0×10^3; 3 = 5.0×10^2 poly(butadiene)

(B) 1 = 2.6×10^5; 2 = 3.3×10^4; 3= 1.3×10^3 poly(isoprene)

(C) 1 = 6.4×10^5; 2 = 1.2×10^4 poly(methyl methacrylate)

(D) 1 = 7.3×10^4; 2 = 9.2×10^3; 3 = 6.3×10^2 poly(ethylene glycol/oxide) cative of the resolving power of the technique (i.e., the greater the distance between two curves, the better TLC resolutions are obtained). There is an apparent deviation in the behavior of the higher molecular weight poly(ethylene glycol/oxide) polymers when the mobile phase contains an excess of the good solvent (Figure 6D). The lower R_f values in this region are thought to be due to a slight adsorption of the polymer to the stationary phase. This adsorption may be due to the presence of a small number of residual silanol groups or possibly to the binder present in the TLC plate. Regardless of the source of the binding, the presence of a small amount of the poor solvent, preferentially interacting with these adsorption sites, releases the polymer. After release, the behavior of the poly(ethylene glycol/oxide) is analogous to that of the other polymers (Figures 6A, B and C).

THEORY

A theory has been developed for a chromatographic model system which accounts for many of the phenomena observed in this work (2). The model system assumes an equilibrium distribution of isolated flexible polymer molecules between a binary solvent mobile phase and a planar stationary phase. In the mobile phase the polymer is assumed to be a spherical gel having a uniform segment density. On the stationary phase the polymer assumes a flat, thin cylindrical conformation. For polymers of sufficiently high molecular weights, there is a critical mobile phase mole fraction, X_{1mc}, of the more favorable, less polar solvent 1 such

Figure 7: Illustration of the two theoretically possible configurations for a high molecular weight polymer in reversed phase TLC or LC gradient fractionation.

that when $X_{1m} > X_{1mc}$ the polymer will move at the same rate as the mobile phase while when $X_{1m} < X_{1mc}$ the polymer is completely retained by the stationary phase (see Figure 7). The critical composition is dependent on molecular weight. This dependence results from the flexibility of the polymer which enables it to change configuration in response to its environment. As a result of the X_{1mc}-molecular weight dependence, one can chromatographically fractionate homopolymers with gradient elution techniques (2). In the TLC fractionation described in this work, for example, the mobile phase changes composition continuously during development as a result of selective adsorption of the better solvent by the stationary phase. To achieve fractionation via this method one must carefully choose a good-poor solvent pair that will interact differently with the stationary phase and produce the optimum gradient.

One can obtain the theoretical expression for the capacity factor of a polymer using the Flory-Huggins lattice model for isolated polymer-solvent systems in both the mobile and stationary phases, as well as the Bragg-Williams approximation for the nearest neighbor interactions (2-4). From the expression for the capacity factor one can obtain equations relating retention time (in LC) and R_f (in TLC) to polymer molecular weight (vide infra).

$$t_r = t_m + B^{-1}(X_{1mc} - X_{1m(o,o)}) + (|A_1| MB)^{-1}\ln(|A_1| MBt_m) \qquad (1)$$

where t_r = retention time of polymer, t_m = retention time of an unretained solute, X_{1mc} = critical solvent composition for a polymer, $X_{1m(o,o)}$ = initial mobile phase composition, B = rate at which the mobile phase composition varies, A = a constant dependent on solvent-solvent and solvent-polymer interchange energies, and M = degree of polymerization.

$$R_f = (|A_1| Mk\tfrac{L}{u})^{-1}\ln[1 + (|A_1| Mk\tfrac{L}{u})\exp[|A_1| M(X_{1m(o)} - X_{1mc})](1 - R_f)] \qquad (2)$$

where: k = rate constant indicative of the change in mobile phase composition. In the above case the rate law is considered to be independent of the composition of the better polymer solvent. $X_{1m}(o)$ = composition of the mobile phase in the reservoir of the development tank, L = distance advanced by the solvent front and u = average rate of migration of the solvent front.

Equations 1 and 2 describe analogous processes. The main difference is that in LC separations, (equation 1) fractionation occurs by going from a poor to a good mobile phase, while in TLC (equation 2) fractionation occurs by going from a good to a poor mobile phase as the chromatogram develops. In both cases the relationship between the mobile phase composition and the critical composition controls the elution of a polymer.

Both equations 1 and 2 can be used to predict qualitative chromatographic trends. The closest correlation between theoretical and experimental values (of t_r and R_f) is for the higher molecular weight polymers (2). As one can see in Figure 6, the concept of a critical concentration is most accurate for the higher molecular weight polymers. For lower molecular weight polymers there can be an appreciable transition range in which the polymer elution behavior varies over a wide range of solvent compositions (Figure 6). In these cases one can envision more gradual transitions from the desorbed to adsorbed state (Figure 8). Prediction of retention times from equation (1) tends to be more accurate than the prediction of R_f values from equation 2 (2).

Figure 8: Illustration of the change of configuration of a polymer which occurs in the transition region (i.e., that region where polymers are not completely adsorbed or desorbed). The range of the transition region increases as a polymer's molecular weight decreases.

The major reason is believed to be that the solvent gradient is known and exactly controlled in LC but not in TLC. In addition, TLC is subject to changing phase ratios, wetting phenomena, etc. Despite these deficiencies, the major theoretical trends are consistant with experimental observation.

Equation 2 can be solved directly (2); however, it is somewhat cumbersome and difficult to visualize in terms of experimental results presented here. Fortunately, one can simplify the expression to a more understandable form when analyzing certain special cases. For all but lower molecular weight polymers (where $X_{1m(o)} - X_{1mc} > 0$),

$$(|A_1| M \frac{L}{u}) \exp(|A_1| M(X_{1m(o)} - X_{1mc}))(1 - R_f) \gg 1$$

and equation 2 simplifies to:

$$R_f = \frac{u(X_{1m(o)} - X_{1mc})}{kL} + \frac{u}{|A_1| MkL} \ln(\frac{|A_1| MkL}{u}) + \frac{u \ln(1 - R_f)}{|A_1| MkL} \qquad (3)$$

For moderate to high molecular weight polymers the second and third terms of equation 3 become increasingly small relative to the first term. Therefore, for "high polymers":

$$R_f = \frac{u(X_{1mc(o)} - X_{1mc})}{kL} \qquad (4)$$

When $X_{1m} - X_{1mc}$ is greater than zero (i.e., the mobile phase in the developing chamber is a good solvent), polymer migration will occur. The extent of this migration can be calculated providing the gradient (k) and the critical mobile phase composition (X_{1mc}) are known. X_{1mc} increases monotonically with M and asymptotically approaches a limiting value X_{1mc}^{∞} as $M \rightarrow \infty$. This indicates that chromatographic resolution should decrease as the molecular weight increases.

When $X_{1m(o)} - X_{1mc}$ is less than zero (i.e., the mobile phase in the developing chamber is a poor solvent mixture) then

$$(|A_1| Mk\frac{L}{u})\exp[|A_1| M(X_{1m(o)} - X_{1mc})](1 - R_f) \rightarrow 0$$

for higher molecular weight polymers and $R_f = 0$.

It is apparent that the theoretical description is consistent with experimental observation. The results of this union are threefold:

1. The fractionation mechanism is largely understood.
2. A useful polymer fractionation technique can now be utilized and improved systematically.
3. The use of TLC and LC can now be used as a potentially powerful tool in the theoretical and physico-chemico study of polymers and their behavior in various environments.

ACKNOWLEDGEMENTS

This work was supported by grants from Whatman Chemical Separation Division and the National Science Foundation

(CHE-8119055) and (CHE-7919322). We gratefully acknowledge their assistance. We also thank Dr. Gerard Kraus of the Phillips Petroleum Company for supplying a poly(butadiene) standard.

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