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Note

Hot thin-layer chromatographic fractionation of polyethylene

D. W. ARMSTRONG* and X. F. YANG

Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65401-1249 (U.S.A.)

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High-performance size-exclusion chromatography (HPSEC) is the predominant chromatographic method used to analyze polymers. Recently there has been an increased interest in the use of non-aqueous high-performance liquid chromatography (HPLC) and thin-layer chromatography (TLC) methods for the analysis of polymers[1–5]. As a point of departure, this work built upon earlier normal-phase chromatographic results obtained by Inagaki[6], Belenkii and Gankina[7,8], and Otocka[9]. By varying the experimental conditions one can do either qualitative analysis of polymers or separate them by molecular weight[4]. These approaches were shown to have over an order of magnitude more resolving power than conventional size-exclusion methods[10]. In addition, the theory and mechanism of the separation process was elucidated[2,11,12]. It was demonstrated via calculations and experiment that conventional LC partition and kinetic theory for small molecules cannot be applied generally to polymer separations. For binary mobile phases, the concept of a critical mobile phase composition was introduced[2,11,12]. Below this critical composition, no elution occurs while at concentrations above it, there is rapid elution. Factors such as polymer molecular weight and chemical make-up can affect its critical solvent composition. By engineering a system in which strong stationary phase adsorption is minimized one can fractionate polymers by molecular weight[2,4,12]. In the case of silica gel based stationary phases this is done by silanizing all available silanol groups (as in typical reversed-phase media) or by using mobile phases or additives that deactivate the silica gel. Both LC and TLC can be used to fractionate polymers according to molecular weight provided a proper binary solvent combination is used (consisting of a good and poor solvent for the polymer). In addition, polymer fractionation requires gradient elution. In TLC, a gradient can form spontaneously via demixing during development when the stationary phase preferentially adsorbs one component, thereby enriching the mobile phase in the other[1,2].

Crystalline polymers (such as polyethylene and polypropylene) are difficult to analyze by any chromatographic method because they cannot be dissolved easily except at elevated temperatures in certain solvents. Given the problems and cost involved in doing HPSEC it seemed reasonable to examine simpler alternatives. Carrying out TLC separations at elevated temperatures (100–140°C) is one possible alternative that is analyzed in this communication. To our knowledge, there have been no prior reports on using "hot" TLC to fractionate crystalline polymers. When doing experiments of this type, close attention must be paid to safety factors (see cautionary note in the experimental section).

EXPERIMENTAL

Materials

Silica gel TLC plates (KGF, 5 × 20 cm) were obtained from Whatman. Dodecane, hexadecane, diethylmalonate, 1,2,4-trichlorobenzene and polyethylene glycol (MW $\approx$ 400) were obtained from Aldrich. Phenyl ether was obtained from Fisher Scientific and benzyl alcohol from MCB Manufacturing. Polyethylene of molecular weight 2000 was obtained from Polysciences. Polyethylene standards of molecular weight 13 600; 32 000; 52 000 and 119 600 were obtained from the U.S. National Bureau of Standards. All standards were of a narrow molecular weight distribution except for the 52 000 MW standard which had a M_w/M_n of 2.9. All developments were done in 15 cm high × 8.5 cm diameter cylindrical glass jars.

Methods

Each 5 × 20 cm plate was cut in half (to make two 5 × 10 plates). The polyethylene standards were dissolved in a hot solvent such as dodecane and individually spotted one cm from the bottom of the plate. A covered jar containing the binary solvent mobile phase was placed in a heated, insulated chamber at the desired temperature between 110°C and 125°C (to ± 1°C). The spotted TLC plate was placed along side the developing chamber and both were allowed to reach the higher chamber temperature ($\approx$ 30 min). Subsequently, the "hot" TLC plate was placed into the "hot" developing jar. The chromatogram was allowed to develop (30–120 min depending on the mobile phase composition) at the elevated temperature. After development, the solvent was evaporated from the plate in a vacuum oven and the polyethylene spots were visualized using sulfuric acid charring (yellow-brown spots on a white background).

In general, the best binary mobile phase for polyethylene seemed to be 1,2,4-trichlorobenzene and benzyl alcohol. Exact conditions are given in the figure legends and the Results and Discussion section.

Cautionary note

The TLC developing chamber should not be tightly sealed or it could explode upon heating. The TLC development should not be done in an oven with exposed heating coils or any surface that could cause catalytic decomposition of the organic vapors, otherwise ignition could occur. All vapors from the experiment should be properly ventilated. When using high-temperature TLC, it is advisable to use solvents with low vapor pressures, high boiling points and high flash points.

RESULTS AND DISCUSSION

The TLC fractionation of polymers by molecular weight is most effective on reversed-phase plates[1,4]. This is because silanization eliminates most of the "strong adsorption sites" and strong adsorption tends to accentuate separations based on differences in chemical composition and structure rather than molecular weight. Unfortunately, it was difficult to visualize polyethylene on reversed-phase TLC plates. For example, sulfuric acid charring methods affected the hydrocarbon C_{18} stationary phase as much as the hydrocarbon polymer. Hence, it was necessary to use normal-
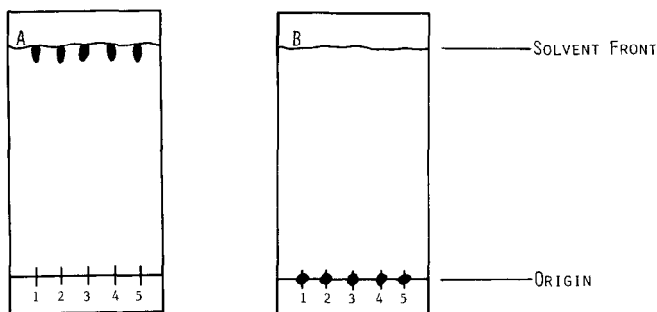
Fig. 1. (A) Schematic of TLC plate after development at 125°C with a pure good solvent (*i.e.*, 1,2,4-trichlorobenzene, diethyl malonate or hexadecane). All polyethylene standards travel with the solvent front ($R_F = 1$). (B) An analogous chromatogram in which neat, poor solvents were used as mobile phases (*i.e.*, benzyl alcohol, polyethylene glycol, or phenyl ether). In this case there is no movement of any polymer ($R_F = 0$). The molecular weight of the polyethylene standards are: (1) 2 000; (2) 13 600; (3) 32 100; (4) 52 000 and (5) 119 600.

phase silica gel TLC plates. Previously, it was demonstrated that a rough molecular weight dependence for polystyrene could be seen on silica gel if the appropriate mobile phase was chosen[6,9]. In general, this means that a component of the mobile
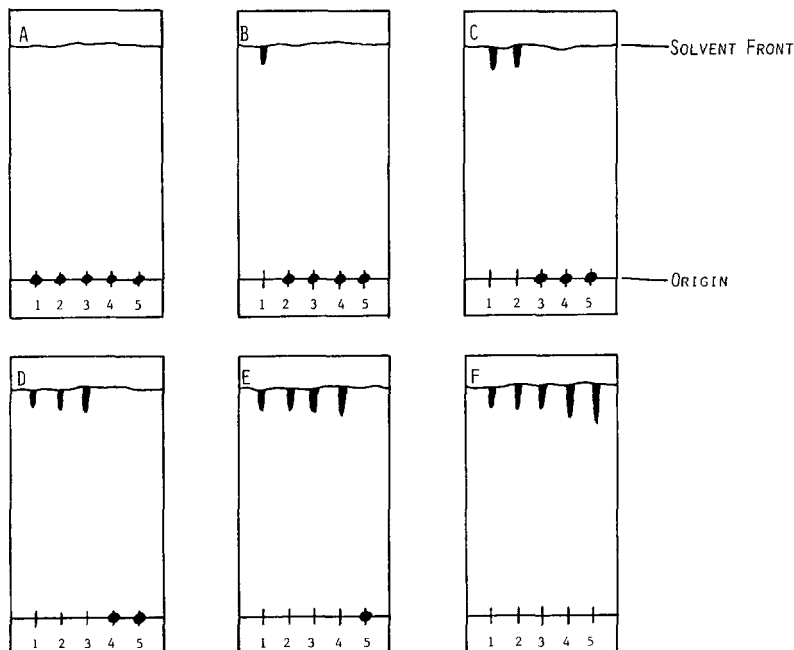

Fig. 2. Schematic showing the effect of mobile phase composition on elution of different molecular weight polyethylenes on silica gel TLC plates. The mobile phase consisted of various mixtures of the good–poor solvent pair, 1,2,4-trichlorobenzene–benzyl alcohol. The molecular weight of each polymer (1–5) is the same as indicated in Fig. 1. The volume percent of 1,2,4-trichlorobenzene in each chromatogram was: (A) 1%, (B) 25%, (C) 45%, (D) 52%, (E) 60% and (F) 75%.

phase must be more polar (and therefore more strongly adsorbed) than any segment of the polymer.

As in previously reported TLC polymer fractionation techniques, a binary good–poor solvent pair is used as the mobile phase. When using the pure good solvent as the mobile phase at 125°C, polyethylenes of all molecular weights move with the solvent front (Fig. 1A). Conversely, when neat poor solvents are used, under identical conditions, there is no movement from the origin (Fig. 1B). By mixing the good and poor solvents in various proportions, polymers of different molecular weight can be moved. For each molecular weight polymer, there is a critical mobile phase composition. This molecular weight-critical composition dependence arises from the flexibility of the polymer which enables it to change configuration in response to its environment[2,4,11,12]. Fig. 2 shows the effect of mobile phase composition on the movement of polyethylene polymers of different molecular weight. As the volume percent of the good solvent (1,2,4-trichlorobenzene) increases, higher-molecular-weight polymers elute with the solvent front (Fig. 2). In the case of polymers with a wider molecular weight range (such as the 52 000 MW polyethylene standard) a mobile phase can be used which causes the lower MW species to move while leaving the higher MW species at the origin.

There are two ways to obtain a chromatogram in which each molecular weight polymer has a slightly different R_F (as has been done for non-crystalline polymers[1,2]). The first way is to use gradient-elution TLC[9]. The second is to use a reversed-phase plate that forms its own gradient during development[1,4]. The former technique has already been described in the literature. The latter approach requires the use of reversed-phase plates and therefore awaits a solution to the visualization problem (*vide supra*).

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