

Short communication

Size-exclusion chromatography of nylons in methylene chloride–dichloroacetic acid

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Abstract

Methylene chloride–dichloroacetic acid (80:20, v/v) is used as a room-temperature size-exclusion chromatography eluent for a variety of nylons. The eluent was previously shown to be suitable for poly(ethylene terephthalate), and this application shows its utility for other polymer classes that are difficult to solubilize. Absolute molecular masses are measured by low-angle light-scattering detection, and a means is provided for generating narrow-standard calibration curves from polystyrene standards.

1. Introduction

Four approaches have been taken in the characterization of nylons by size-exclusion chromatography (SEC):

(1) High-temperature SEC in phenolic solvents [1–3], benzyl alcohol [4–6] or hexamethylphosphoramide [7–9].

(2) SEC in common solvents such as tetrahydrofuran after solubilization by trifluoroacetylation [10–16].

(3) SEC in fluorinated alcohols such as trifluoroethanol [17–22] and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) [9,23–25].

(4) SEC at room temperature in mixed solvents such as *m*-cresol–chlorobenzene [3] or HFIP–toluene [26].

Each approach has advantages and disadvantages

discussed in most of the papers referenced above. Methylene chloride–dichloroacetic acid (DCAA) (80:20, v/v), containing 0.01 *M* tetrabutylammonium acetate (TBAA) is an alternative for room-temperature SEC of crystalline polyesters such as poly(ethylene terephthalate) (PET) [27]. The solvent pair is nearly isorefractive, allowing the use of light-scattering detection. It does not significantly degrade PET, polystyrene standards are suitable for calibration, it is used at room temperature, and it is comparatively inexpensive. Application to nylons is a logical and practical extension of its use; some of these polyamides are soluble only in solvents that dissolve PET. The intent of this study is to evaluate this eluent originally developed for PET, without modification, with the practical objective of using the same solvent and SEC system for both crystalline polyesters and polyamides.

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2. Experimental

2.1. Sample preparation

Narrow molecular mass distribution polystyrenes were obtained from Polymer Labs. (Amherst, MA, USA). Nylon 6,6, 46K and 32K standards were obtained from American Polymer Standards (Mentor, OH, USA). All other nylon samples were obtained from Scientific Polymer Products (Ontario, NY, USA). Typically, 25 mg of nylon were dissolved at room temperature in the SEC eluent containing 0.01% 1-chloro-2,4-dinitrobenzene as a flow marker.

2.2. Size-exclusion chromatography

The SEC was similar to that described for PET [27]. Eluent was methylene chloride–DCAA (80:20, v/v) containing 0.01 M TBAA. The nominal flow-rate was 1.0 ml/min, and sample injection volumes were 100 μ l. A Spectroflow 757 UV detector operating at 310 nm, an LDC Analytical KMX-6 low-angle laser-light-scattering (LALLS) photometer, and a Waters Model 401 differential refractive index (DRI) detector were connected in series after the columns. The SEC columns and DRI detector were thermostated to 30.0°C. The UV and LALLS detectors were operated at room temperature. All light-scattering intensities were measured at 6–7° with an aperture of 0.15 mm. Flow-rates were corrected using the UV chromatogram and the retention volume of the 1,2-chloro-2,4-dinitrobenzene flow marker.

3. Results and discussion

3.1. Dissolution and solution properties

Nylon pellets dissolve in the methylene chloride–DCAA (80:20) eluent at room temperature in less than 1 h at a concentration of 2.5 mg/ml. There is no evidence for phase separation at this polymer concentration, even after several days in solution. Dilute solution viscosity is adequately fitted by the conventional relationships of

specific, η_{sp} , and reduced, η_r , viscosity with concentration, c :

$$\eta_{sp} = [\eta]c + k'[\eta]^2c^2 \quad (1)$$

$$\ln \eta_r = [\eta]c + k''[\eta]^2c^2 \quad (2)$$

The intrinsic viscosity $[\eta]$ of a nylon 6 sample with weight-average molecular mass of 24 800 is 0.643 dl/g, $k' = 0.39$ and $k'' = -0.13$. It is possible to use less DCAA acid for SEC; nylon 6, 6/6, 6/9, 6/10, and 6/12 are soluble at a concentration of 2.5 mg/ml in dichloromethane containing 5% (v/v) DCAA. Nylon 11 and nylon 12 require a minimum of approximately 10% dichloroacetic acid. SEC results in these eluent compositions have not been investigated extensively; instead, our objective is to show the general utility of a single solvent system (methylene chloride–DCAA, 80:20) for both crystalline polyesters and nylons.

3.2. Chromatography

Typical LALLS and DRI chromatograms of nylon 6,6 are shown in Fig. 1. A small peak in the DRI chromatogram from TBAA appears near the solvent peaks. This salt eliminates polyelectrolyte effects in polar solvents and is necessary for reproducible elution of PET. Its necessity for nylons has not been established. The salt does not absorb above 300 nm and the interference is not observed with a UV detector

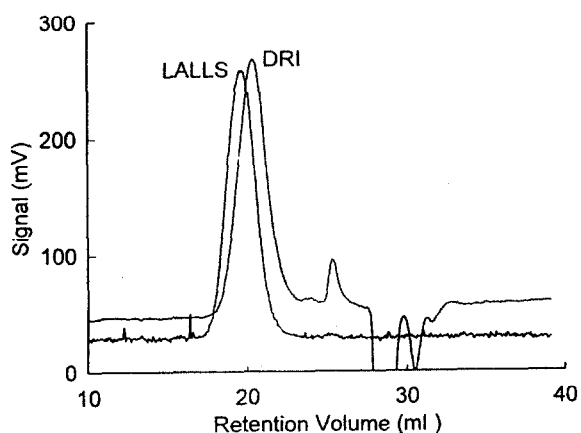


Fig. 1. LALLS and DRI chromatograms of nylon 6,6 46K.

for PET and nylon 6T. However, UV detection cannot be used with this solvent for aliphatic nylons, and the low-molecular-mass information (e.g., number-average molecular mass) obtained from the DRI is limited if the salt is present. A similar problem exists with SEC of aliphatic nylons in HFIP with sodium trifluoroacetate [9].

Previous experience with PET suggests that sample degradation is most likely at high temperatures, with water concentrations greater than 1% (v/v), and with standing in the eluent for greater than four days. Degradation or transamidation is also a concern for nylons in an acidic eluent. There is no discernible difference in the normalized chromatograms of nylon 6 samples that sat for 48 h in the eluent at room temperature. Unlike PET, there is also no change in nylon 6 after exposure for 48 h to eluent containing 4% water. Stability at high temperatures is not an issue since all nylon samples are dissolved and analyzed at room temperature. The results show that sample degradation in the eluent is less important for nylons than for PET.

3.3. Specific refractive index increment

The specific refractive index increment of nylon samples is estimated from the differential refractometer response by the method of Berkowitz [28]. This method was successfully applied to PET in this eluent [27]. We note that the

differential refractometer used in the previous study (Waters Model 410) developed leaks around the inlet fittings after approximately nine months of continuous use. The older and simpler Waters Model 401 has fewer inlet fittings and is a sturdier substitute with this eluent, which is corrosive to some stainless-steel ferrules. Specific refractive index increments of nylons are given in Table 1.

3.4. Light-scattering detection

Absolute molecular masses are calculated from the excess Rayleigh scattering, $R_{\theta,i}$ and the signal from a concentration detector (either UV or DRI) c_i at each eluting slice i ,

$$\frac{Kc_i}{R_{\theta,i}} = \frac{1}{M_{w,i}P(\theta)_i} + 2A_2c_i + 3A_3c_i^2 + \dots \quad (3)$$

where K is the light-scattering optical constant, $P(\theta)_i$ is the particle scattering function and A_2 and A_3 are virial coefficients. The weight-average molecular mass (M_w) of the whole polymer (values reported in Table 1) is obtained from either the light-scattering signal alone (no DRI) or from summation of the molecular masses and concentrations at each slice i of the chromatogram, as described in Ref. 27. Results reported in Table 1 are from integration of the light-scattering chromatograms (no DRI). Precision is comparable to that obtained for PET. There is

Table 1
SEC-LALLS of nylons

Sample	No. of samples	dn/dc^a (ml/g)	M_w^b	β_1	β_2
Nylon 6	10	0.180 ± 0.006	24 800 ± 1000	-0.372	1.005
Nylon 6,6 46K	10	0.188 ± 0.008	41 400 ± 1300	-0.758	1.067
Nylon 6,6 32K	10	0.194 ± 0.007	31 100 ± 900	-0.379	1.001
Nylon 6,6	8	0.182 ± 0.012	33 000 ± 1300	-0.657	1.053
Nylon 6,9	10	0.163 ± 0.002	30 500 ± 1200	-0.678	1.082
Nylon 6,10	4	0.163 ± 0.002	33 700 ± 450	-0.703	1.094
Nylon 6,12	10	0.149 ± 0.002	25 700 ± 700	-0.128	0.963
Nylon 11	6	0.133 ± 0.002	26 000 ± 900	-1.339	1.197
Nylon 12	6	0.133 ± 0.004	28 200 ± 900	-0.460	1.009
Nylon 6T	8	0.201 ± 0.003	36 800 ± 400	-0.403	1.021

^a Specific refractive index increment.

^b Weight-average molecular mass from SEC-LALLS.

reasonable agreement with vendor values for nylon 6,6 with weight-average molecular masses of 46 000 (46K) and 32 000 (32K).

3.5. Calibration curves from light-scattering detection

Size-exclusion calibration curves can be established from the relationship between nylon molecular mass, M_2 , and standard molecular mass, M_1 ;

$$\log M_2 = \beta_1 + \beta_2 \log M_1 \quad (4)$$

The constants β_1 and β_2 are obtained by plotting the polystyrene $\log M$ -retention volume calibration curve versus the $\log M$ -retention volume curve for nylon measured by light-scattering detection [29]. A similar approach has been used to convert poly (methylmethacrylate) (PMMA) equivalent molecular masses to nylon molecular masses in HFIP with supporting electrolyte [30]. Viscosity measurements and direct application of universal calibration are not required. Calibration curves for nylons are obtained by calibrating the column set with narrow molecular mass distribution polystyrene stan-

dards. Polystyrene molecular masses are converted to nylon molecular weights using Eq. 4 and the constants provided in Table 1. A typical nylon 6,6 calibration curve is compared to polystyrene in Fig. 2. This calibration curve allows calculation of absolute molecular mass distributions from a concentration detector only.

4. Discussion

The eluent composition is optimized for PET and related crystalline polyesters and may not be optimized for nylons. As evaluated, the eluent is compared with the four other approaches for the SEC of nylons:

(1) Operation at room temperature is desirable. There is also no evidence for polymer degradation; this is a concern in phenolic solvents at high temperatures.

(2) There is no derivatization step. In the case of trifluoroacetylation, some workers have cited differences in results depending on the degree of acetylation and complications in the calculation of molecular masses by universal calibration [12,14]. Trifluoroacetyl derivatives are also sensitive to moisture and the eluents must be carefully dried.

(3) The solvent is less expensive than fluorinated solvents. However, it causes skin burns and it is corrosive to stainless steel after long-term use. Typically, connecting tube fittings (especially ferrules) and pump parts will require replacement after 6–9 months of continuous use. We have been unsuccessful using viscometry detection because of flow fluctuations that develop from minor leaks in and about viscometer detectors. It is noted, however, that fluorinated solvents such as HFIP also pose significant safety hazards, particularly to the eyes.

(4) Criticism of mixed solvents, including sensitivity to changes in eluent composition, selective solvation and complications with light-scattering detection and DRI baseline stability are minimized with methylene chloride–DCAA. There is little difference in chromatograms obtained at 20% and 10% DCAA [27], and the solvent pair is nearly isorefractive, making it

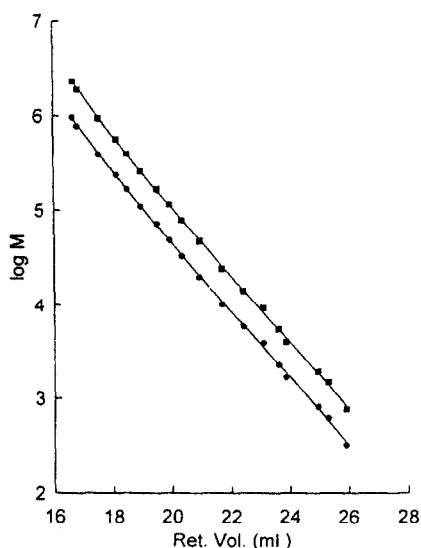


Fig. 2. Narrow standard calibration curves for (■) polystyrene and (●) nylon 6,6.

suitable for light-scattering. Acceptable DRI baselines are easily established and remain stable. Specific refractive index increments in this eluent are lower than in fluorinated solvents such as HFIP, thereby reducing the sensitivity of light-scattering detectors. However, it is relatively easy to obtain low scattering background with the higher solvent refractive index and LALLS cell windows require infrequent cleaning.

5. Conclusions

The methylene chloride–DCAA eluent used for crystalline polyesters such as PET can also be used for the SEC of nylons at room temperature. There is no evidence for degradation of nylons in this solvent, and absolute molecular masses are obtained from light-scattering detection. To its disadvantage, the low-molecular-mass region is difficult to quantitate in aliphatic nylons because of interference from TBAA.

References

- [1] M.A. Dudley, *J. Appl. Polym. Sci.*, 16 (1972) 493.
- [2] Z. Tuzar, P. Kratochvíl and M. Bohdaneck, *Adv. Polym. Sci.*, 30 (1979) 117.
- [3] P.S. Ede, *J. Chromatogr. Sci.*, 9 (1971) 275.
- [4] G. Pastuska and U. Just, *Angew. Makromol. Chem.*, 81 (1979) 11.
- [5] G. Pastuska, U. Just and H. August, *Angew. Makromol. Chem.*, 107 (1982) 173.
- [6] G. Marot and J. Lesec, *J. Liq. Chromatogr.*, 11 (1988) 3305.
- [7] D. Petit, R. Jerome and Ph. Teyssie, *J. Polym. Sci., Polym. Chem. Ed.*, 17 (1979) 2903.
- [8] R. Panaris and G. Pallas, *J. Polym. Sci., Polym. Lett.*, 8 (1970) 441.
- [9] D.J. Goedhart, J.B. Hussem and B.P.M. Smeets, in J. Cazes (Editor), *Liquid Chromatography of Polymers and Related Materials (Chromatographic Sciences Series, Vol. 13)*, Marcel Dekker, New York, 1977, p. 203.
- [10] H. Schuttenberg and R.C. Schulz, *Angew. Chem.*, 88 (1976) 848.
- [11] E. Jacobi, H. Schuttenberg and R.C. Schulz, *Makromol. Chem. Rapid Commun.*, 1 (1980) 397.
- [12] E. Biagini, E. Gattiglia, E. Pedemonte and S. Russo, *Makromol. Chem.*, 184 (1983) 1213.
- [13] K. Weiskopf and G. Meyerhoff, *Polymer*, 24 (1983) 72.
- [14] K. Weiskopf, *Polymer*, 26 (1985) 1187.
- [15] T. Ogawa and M. Sakai, *J. Liq. Chromatogr.*, 8 (1985) 1025.
- [16] T. Ogawa and M. Sakai, *J. Polym. Sci.: Part A: Polym. Chem. Ed.*, 26 (1988) 3141.
- [17] G. Costa and S. Russo, *J. Makromol. Sci., Chem. Ed.*, A18 (1982) 299.
- [18] T. Provder, J.C. Woodbrey and J.H. Clark, *Sep. Sci.*, 6 (1971) 101.
- [19] T. Provder, J.C. Woodbrey, J.H. Clark and E.E. Drott, *Adv. Chem. Ser.*, 125 (1973) 117.
- [20] M. Matzner, L.M. Robeson, R.J. Gref and J.E. McGrath, *Angew. Makromol. Chem.*, 26 (1972) 137.
- [21] P.J. Wang and R.J. Rivard, *J. Liq. Chromatogr.*, 10 (1987) 3059.
- [22] C.A. Veith and R.E. Cohen, *Polymer*, 30 (1989) 942.
- [23] E.E. Drott, in J. Cazes (Editor), *Liquid Chromatography of Polymers and Related Materials (Chromatographic Sciences Series, Vol. 13)*, Marcel Dekker, New York, 1977, p.41.
- [24] H. Schorn, R. Kosfeld and M. Hess, *J. Chromatogr.*, 282 (1983) 579.
- [25] S.R. Samanta, *J. Appl. Polym. Sci.*, 45 (1992) 1635.
- [26] T. Ogawa, M. Sakai and W. Ishitobi, *J. Polym. Sci.: Part A: Polym. Chem. Ed.*, 24 (1985) 109.
- [27] T.H. Mourey, T.G. Bryan and J. Greener, *J. Chromatogr. A*, 657 (1993) 377.
- [28] S.A. Berkowitz, *J. Liq. Chromatogr.*, 6 (1983) 1359.
- [29] T.H. Mourey and S.T. Balke, *J. Appl. Polym. Sci.*, submitted for publication.
- [30] S. Mori and Y. Nishimura, *J. Liq. Chromatogr.*, 16 (1993) 3359.