polymer report

Refractive index of poly(thiocarbonate)s and poly(dithiocarbonate)s

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The refractive indices and densities of recently synthesized poly(thiocarbonate)s and poly(dithiocarbonate)s were measured, and were used to determine the group contributions of thiocarbonate (–O–CO–S–) and dithiocarbonate (–S–CO–S–) groups to the molar refraction. The high refractive indices observed make these polymers, particularly the poly(dithiocarbonate)s, potentially interesting for optical applications (i.e. lenses and optical fibres).

(Keywords: poly(thiocarbonate)s; poly(dithiocarbonate)s; refractive index)

INTRODUCTION

In a series of recent papers we reported the synthesis and characterization of new polymers containing thiocarbonate (–O–CO–S–) or dithiocarbonate (–S–CO–S–) groups, which were obtained by reacting aromatic or aliphatic dithiols with phosgene and/or chlorocarbonyloxy groups. The substitution of oxygen atoms for sulfur atoms results in significant differences between the properties of poly(carbonate)s and poly(thiocarbonate)s or poly(dithiocarbonate)s, for instance in the thermal behaviour[1–10].

The optical properties may be very important in many applications (i.e. lenses and optical fibres); for these classes of polymers no data are available in the literature. The aim of this study was to evaluate the refractive index of these polymers and determine the contributions of thiocarbonate and dithiocarbonate groups to molar refraction, which can be used to estimate the refractive index values of polymers containing these groups, on the basis of their chemical structure.

EXPERIMENTAL

Polymers

The polymers studied in this work were prepared by interfacial synthesis and were characterized for molecular and thermal properties as previously described[4–10].

Refractive index measurements

Refractive indices were measured at 23°C with an Abbé refractometer (equipped with Na lamp) on thin films which were obtained by casting the polymers, in chloroform solutions, directly onto the prism of the refractometer.

Density measurements

Densities were measured by the flotation method in the system of aqueous KI solution (40% w/w, density 1.398 g cm^{-3}) and water; 11 commercial glass beads of known density in the range 1.0578–1.3523 g cm^{-3} were used for calibration.

RESULTS AND DISCUSSION

The experimental data of the molecular and thermal characterization, density and refractive index measurements for four poly(thiocarbonate)s and four poly(dithiocarbonate)s are reported in *Table 1*.

The refractive index values are quite high for all the polymers examined, with maximum values of around 1.68 for the two all-aromatic poly(dithiocarbonate)s, SSBTM and SSBTO.

It is well known[11] that the additive property that correlates refractive index n and density ρ with the chemical structure of a substance is the molar refraction R. The molar refraction may be defined by the Lorentz–Lorenz equation, which has its theoretical basis in the electromagnetic wave theory of light:

$$R_{LL}=\frac{n^2-1}{n^2+2}\frac{M}{\rho}=\sum R_{LL,i} \quad (1)$$

or with two other empirical equations, that of Gladstone and Dale:

$$R_{GD}=(n-1)\frac{M}{\rho}=\sum R_{GD,i} \quad (2)$$

and of Vogel:

$$R_V=nM=\sum R_{V,i} \quad (3)$$

where M is the molar mass (in the case of polymers the molar mass of the repeating unit), and $R_{LL,i}$, $R_{GD,i}$ and

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$R_{V,i}$ are the molar refraction group contributions for equations (1)–(3), respectively.

For the more common atoms, bonds and groups the contributions to the molar refraction are reported in the literature[11]; they were obtained from experimental refractive index values and can be used to predict the refractive index of a new polymer of known chemical structure.

The molar refraction group contributions of (–O–CO–S–) and (–S–CO–S–) are not available at present. We determined these contributions by subtracting those reported by van Krevelen for all the other groups contained in the repeating unit (except thio- or dithiocarbonate) from the molar refraction calculated using experimental values of n and ρ of poly(thiocarbonate)s and poly(dithiocarbonate)s. The results are summarized

Table 1 Intrinsic viscosity, thermal transitions, density and refractive index experimental data

Polymer repeat unit[a]	Code	$[\eta]$[b] (dl g^{-1})	T_g[c] (°C)	T_m[c] (°C)	Density[d] (g cm^{-3})	Refractive index
–[–O–Φ–C(CH$_3$)$_2$–Φ–O–CO–S–(CH$_2$)$_3$–S–CO–]–	OSR3	0.97	90	–	1.255	1.588
–[–O–Φ–C(CH$_3$)$_2$–Φ–O–CO–S–(CH$_2$)$_6$–S–CO–]–	OSR6	0.78	58	–	1.203	1.574
–[–O–Φ–C(CH$_3$)$_2$–Φ–O–CO–S–Φ–C(CH$_3$)$_2$–Φ–S–CO–]–	OSBTA	1.85	154	–	1.194	1.600
–[–O–Φ–C(CH$_3$)$_2$–Φ–O–CO–S–Φ–O–Φ–S–CO–]–	OSBTO	1.78	145	–	1.260	1.621
–[–S–CO–S–(CH$_2$)$_9$–]–	SSR9	0.27	–	91	1.170	1.632
–[–S–CO–S–(CH$_2$)$_{12}$–]–	SSR12	0.22	–	86	1.109	1.604
–[–S–CO–S–Φ–CH$_2$–Φ–]–	SSBTM	0.32	117	–	1.238	1.684
–[–S–CO–S–Φ–O–Φ–]–	SSBTO	0.66	117	–	1.309	1.681

[a] Φ = 1,4-phenylene
[b] In $CHCl_3$ at 30°C
[c] At 20°C min^{-1} scanning rate, under dry nitrogen
[d] At 23°C

Table 2 Molar refractions of polymers and contributions for (–O–CO–S–) and (–S–CO–S–) groups calculated by means of Lorentz–Lorenz, Gladstone–Dale and Vogel equations

	Lorentz–Lorentz equation		Gladstone–Dale equation		Vogel equation	
Polymer code	Molar refraction, R_{LL} (cm^3 mol^{-1})	Thio- or dithio-carbonate group contribution, $R_{LL,i}$ (cm^3 mol^{-1})	Molar refraction, R_{GD} (cm^3 mol^{-1})	Thio- or dithio-carbonate group contribution, $R_{GD,i}$ (cm^3 mol^{-1})	Molar refraction, R_V (cm^3 mol^{-1})	Thio- or dithio-carbonate group contribution, $R_{V,i}$ (cm^3 mol^{-1})
OSR3	104.18	13.30	182.02	23.17	616.93	118.70
OSR6	118.11	13.29	205.45	23.13	677.73	118.13
OSBTA	154.92	13.82	271.70	23.65	865.11	114.93
OSBTO	143.65	14.09	253.63	24.49	834.18	118.38
SSR9	66.58	24.73	117.96	47.48	(356.38)[a]	(170.62)[a]
SSR12	80.78	24.99	141.85	47.88	(417.77)[a]	(170.09)[a]
SSBTM	79.22	24.66	142.74	45.88	435.07	159.20
SSBTO	75.24	23.41	135.43	42.99	437.61	157.81

[a] Vogel equation is not applicable to crystalline polymers, since it does not contain the polymer density

Table 3 Contributions of carbonate (–O–CO–O–), thiocarbonate (–O–CO–S–) and dithiocarbonate (–S–CO–S–) groups

		(O–CO–S–) group		(–S–CO–S–) group	
	(–O–CO–O–) group[a]	Experimental (mean value)	Calculated	Experimental (mean value)	Calculated
$R_{LL,i}$ (cm^3 mol^{-1})	7.74	13.63 ± 0.34[b]	14.14	24.45 ± 0.61[b]	20.54
$R_{GD,i}$ (cm^3 mol^{-1})	13.12	23.61 ± 0.55[b]	24.72	46.06 ± 1.92[b]	36.32
$R_{V,i}$ (cm^3 mol^{-1})	86.8	117.54 ± 1.47[b]	117.3	158.51 ± 0.71[b]	147.8

[a] From reference 11
[b] Standard deviation

in *Table 2*. We observe that the group contributions to the molar refraction for thio- and dithiocarbonate group are quite constant for all the poly(thiocarbonate)s and poly(dithiocarbonate)s examined. In addition, differences in the $R_{LL,i}$, $R_{GD,i}$ and $R_{V,i}$ values between aliphatic and aromatic thiocarbonates or dithiocarbonates are not detectable within experimental error. Some discrepancies observed for samples SSR9 and SSR12, the only two polymers able to crystallize, may be ascribed to the effect of the crystallinity on the density value.

The mean values of these contributions are reported in *Table 3*. They are compared with those calculated simply by adding to the carbonate contribution the difference between the thioethereal sulfur atom and ethereal oxygen atom contributions taken from the literature[11]. It is evident that in the case of the dithiocarbonate group there is a significant positive specific group effect.

In conclusion, the high values of refractive index observed for poly(dithiocarbonate)s make these polymers interesting for optical applications. The recent patent literature reports many examples of sulfur-containing, high refractive index polymers which may be employed for optical materials[12–17].

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REFERENCES

1 Berti, C., Marianucci, E. and Pilati, F. *Polym. Bull. (Berlin)* 1985, **14**, 85
2 Marianucci, E., Pilati, F. and Berti, C. *Polym. Degrad. Stab.* 1986, **16**, 297
3 Pilati, F., Berti, C. and Marianucci, E. *Polym. Degrade. Stab.* 1987, **18**, 63
4 Berti, C., Marianucci, E. and Pilati, F. *Makromol. Chem.* 1988, **189**, 1323
5 Montaudo, G., Puglisi, C., Berti, C., Marianucci, E. and Pilati, F. *J. Polym. Sci. Part A: Polym. Chem.* 1989, **27**, 2277
6 Montaudo, G., Puglisi, C., Berti, C., Marianucci, E. and Pilati, F. *J. Polym. Sci. Part A: Polym. Chem.* 1989, **27**, 2657
7 Pilati, F., Marianucci, E., Berti, C., Manaresi, P. and Della Fortuna, G. *Polym. Commun.* 1990, **31**, 431
8 Berti, C., Della Fortuna, G., Manaresi, P., Marianucci, E., Pilati, F. and Poloni, M. European Patent Application EP 425 049; *Chem. Abstr.* 1991, **115**, 115317
9 Bandiera, M., Berti, C., Manaresi, P., Marianucci, E., Pilati, F. and Poloni, M. *Makromol. Chem.* 1993, **194**, 2453
10 Bandiera, M., Berti, C., Manaresi, P., Marianucci, E., Pilati, F. and Poloni, M. in preparation
11 van Krevelen, D. W. 'Properties of Polymers', Elsevier, Amsterdam, 1990, Ch. 10
12 Masumoto, M., Asao, T., Manabe, Y. and Suzuki, S. Jpn Kokai Tokkyo Koho JP 01 318 065; *Chem. Abstr.* 1990, **113**, 60766r
13 Sakamoto, S., Oshima, K. and Iguchi, Y. Jpn Kokai Tokkyo Koho JP 02 138 316; *Chem. Abstr.* 1991, **114**, 63766a
14 Ohashi, M. and Fukuda, T. Jpn Kokai Tokkyo Koho JP 03 43 415; *Chem. Abstr.* 1991, **115**, 137026
15 Tamura, Y. and Watari, T. Jpn Kokai Tokkyo Koho JP 03 205 413; *Chem. Abstr.* 1992, **116**, 7362s
16 Cho, G., Okubo, T. and Okada, R. Jpn Kokai Tokkyo Koho JP 04 04 211; *Chem. Abstr.* 1992, **116**, 216003q
17 Miyazaki, T. and Murata, T. Jpn Kokai Tokkyo Koho JP 04 11 618; *Chem. Abstr.* 1992, **116**, 257061