

EXTENDED ABSTRACT

Surface characterization of polymers by inverse gas chromatography*

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Abstract: An inverse gas chromatographic (IGC) study of the sorption properties of macroporous crosslinked poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate), PGME, and PGME modified with ethylene diamine, PGME-en, was presented. At infinite dilution, the thermodynamic parameters of adsorption, the dispersive components of the surface free energies, the acid/base constants and the interaction parameters for the initial and modified copolymer samples were investigated. The adsorption isotherms determined by IGC under conditions of finite surface coverage were used to estimate the surface area, the isosteric heat of adsorption and the adsorption energy distribution on the surface of the initial and modified copolymer samples.

Keywords: IGC, glycidyl methacrylate based copolymers, acid/base properties, interaction parameters.

The IGC method has been extensively used for the investigation of the structure of polymers, interactions of various liquids and gases with polymeric materials, as well as polymer–polymer miscibility.¹ The method being simple, relatively rapid, with good accuracy, low cost and readily available equipment provides valuable thermodynamic information for the physico-chemical characterization of polymers. Also, the advantage of IGC is that it allows the examination of different porous materials, the surface properties of which can hardly be determined by other methods, such as contact angle measurements. In this paper, the possibility of polymer characterization by IGC is illustrated with a study of the sorption properties of macroporous crosslinked poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate), PGME, and PGME modified with ethylene diamine, PGME-en.

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The measurements were carried out at zero surface (Henry's law region or infinite dilution region) and at finite surface coverage (finite concentration region). The sorption properties of the copolymer samples were determined using a Hewlett-Packard 5890 Series II gas chromatograph, with a flame ionization detector (FID) maintained at 523 K, with the injector at 493 K. Dry nitrogen was used as the carrier gas (flow rate in the range 25–28 cm³ min⁻¹). Methane was used to determine the dead volume. A stainless steel column (50 cm long, 2.2 mm I.D.) was packed with either the initial or the modified copolymer samples (fraction with particle size of 150–500 μm). After packing, the column was conditioned overnight at 363 K in a stream of nitrogen (flow rate: 5 cm³ min⁻¹). Retentions of organic compounds of different chemical nature and polarity (non-polar, donor or acceptor) were measured in the temperature range 333–413 K. Software Varian Star 4.5 software was employed for data acquisition. Relevant IGC results collected from the retention data were calculated by a Matchad program developed for the purpose.

IGC MEASUREMENTS UNDER INFINITE DILUTION

In the case of IGC measurement at infinite dilution, minor amounts of vapors of the test solutes are injected into the column filled with polymer, permitting the lateral interactions between the adsorbed molecules to be neglected and the retention volumes are independent of the injection sample size. The analysis of the adsorption properties of macroporous crosslinked PGME and copolymers with attached ethylene diamine, PGME-en, is particularly interesting, bearing in mind their use in biotechnological and biomedical applications, heavy and platinum metal sorption, catalysis *etc.*^{2–4} Yet, only a few data regarding the surface properties of PGME have been published,⁵ with no data having been found in the literature on the surface properties of PGME-en, in terms of Lewis acid/base properties and surface free energy.

Adsorption properties of this macroporous PGME samples and corresponding PGME-en samples were investigated by IGC at infinite dilution, in the temperature range 333–363 K. Chemical modification of PGME with ethylene diamine leads to different chromatographic behaviors of the modified and the initial copolymer samples, *i.e.*, to a shortening of the retention of all adsorbates for the modified samples.⁶ The calculated values for the entropy changes of adsorption of the investigated adsorbates are of the same order as those obtained experimentally for all copolymer samples. The differences observed between the experimental and the predicted entropy changes, *i.e.*, an additional entropy loss found experimentally, may result from the restricted rotational and vibrational freedom of adsorbates on the copolymer surfaces. For all the samples, the dispersive surface energy, γ_s^d , gradually decreased with increasing temperature. The calculated γ_s^d values for PGME and PGME-en are in the range 27–48 mJ m⁻² which are comparable with literature data for non-conducting polymers, with the exception of the PGME sample with

the lowest specific surface area, S_a , value. In some cases, such as heterogeneous high-energy surfaces, microporous and lamellar materials, in the presence of impurities, *etc.*, IGC yields higher dispersive surface energy values than other techniques. Bearing this in mind, the overestimated γ_s^d value might be attributed to the different internal structure and possible microporosity of this sample.

Following the Saint-Flour and Papirer approach,⁷ the overall acid/base character of PGME and PGME-en was evaluated from the K_D/K_A ratio (base constant, K_D and acid constant, K_A). Both the initial and modified copolymers have basic character ($K_D/K_A > 1$), which is much more pronounced in the case of the PGME-en samples (K_D/K_A values: 9.0 and 14.5, respectively). The porosity parameters of crosslinked macroporous copolymers influence the accessibility of the acidic and basic sites and, consequently, the Lewis acid/base properties of the copolymer.

The IGC technique was also applied for the determination of some thermodynamic properties of macroporous crosslinked PGME and PGME-en, such as weight fraction activity coefficients of the tested sorbates at infinite dilution, the Flory-Huggins interaction parameters, χ_{12}^∞ , the partial molar free energy, the partial molar heat of mixing, the free energy, enthalpy and entropy of sorption with sorbates of different chemical nature and polarity.⁸ According to the Flory-Huggins interaction parameter, X_{12}^∞ , benzene is a non-solvent, whereas *n*-alkanes, cyclohexane, chloroform, ethyl acetate, diethyl ether, and tetrahydrofuran are good solvents for PGME in the temperature range 403–413 K. For PGME-en, *n*-alkanes, cyclohexane and benzene are non-solvents, while chloroform, ethyl acetate, diethyl ether, and tetrahydrofuran are good solvents in the temperature range 383–413 K.

IGC MEASUREMENTS UNDER FINITE COVERAGE

In the finite concentration (IGC-FC) mode, measurable amounts of solutes are injected, leading to skewed chromatographic peaks. The retention volumes are dependent on the adsorbate concentration in the gas phase. From the peak shapes, adsorption isotherms and the adsorption energy distribution can be calculated.

The adsorption of hexane, chloroform, benzene and tetrahydrofuran was used for the surface analysis of the macroporous crosslinked PGME and PGME-en, in the temperature range 333–363 K.⁹ The adsorption of organic adsorbates on the initial and modified copolymer samples was analyzed using the BET theoretical model. It was shown that the nature of the adsorbate and the properties of the solid surface of the initial and modified copolymer govern the uptake of adsorbate by the copolymer. The average values of specific surface area, S_a , for the investigated adsorbates calculated from hexane IGC data are not in good agreement with those determined by the BET method from low-temperature N_2 adsorption isotherms. The deviations observed for the S_a values obtained with N_2 and hexane can be attributed not only to the difference in the molecule size, but also to specific polymer-adsorbate interactions. The isosteric heat of adsorption approaches a constant

value with increasing adsorbate loading. A large variation in the shapes of the $q_{st}-\alpha$ curves results from the strong acid–base forces, as well as dissolution phenomena. Of the four studied adsorbates, chloroform was shown to have the greatest affinity for the surface of the investigated polymer samples.

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ИЗВОД

ИСПИТИВАЊЕ ПОВРШИНСКИХ СВОЈСТАВА ПОЛИМЕРА ИНВЕРЗНОМ ГАСНОМ ХРОМАТОГРАФИЈОМ

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На примеру одређивања површинских карактеристика макропорозног умреженог поли(глицидилметакрилат-*co*-етиленгликолдиметакрилата), PGME, као и кополимера модификованог са етилендиамином, PGME-ен, приказана је могућност коришћења инверзне гасне хроматографије (IGC) за карактеризацију полимера. При нултој прекривености одређени су термодинамички параметри адсорпције, дисперзивна компонента слободне површинске енергије, кисело/базна својства и параметри интеракције основног и модификованог кополимера. Адсорпционе изотерме одређене при коначној прекривености коришћене су за одређивање специфичне површине, изостеричне топлоте и расподеле адсорпционе енергије на површини основног и кополимера модификованог са етилендиамином.

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