Structure-Property Relationships for Film-Forming Poly(amide imide)s

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SUMMARY: Poly(amide imide)s from dichloro-dianhydrides of tri-mellitimide- and/or pyromellitimide-N-acetic acids (TMA and PMA), linear aromatic dimimines (LAD) and/or cardo diamine (CDA), 9,9'-bis-phenylfluorene (series PAI-1); a similar series (PAI-II) from dichloro-dianhydride of trimellitimide-N-benzoic acid (TMB), LAD and/or CDA ; and a series of coPAIs from dichloro-dianhydride of TMA and mixtures of diphenylmethane diamine (DPA) with CDA were synthesized by low-temperature reaction in dimethyl acetamide (DMAA).
The state of aggregation of PAIs and coPAIs in dilute and semi-dilute solutions of DMAA was characterized by measurements of specific heat capacity in the temperature interval 150-370 K, of heats of dilution in DMAA at room temperature, and of apparent viscosity in the temperature interval 288-373 K.
The state of aggregation of PAIs and coPAIs in thin films cast from DMAA solutions was characterized by wide-angle and small-angle X-ray diffraction, dynamic mechanical analysis, broad-band dielectric spectroscopy and gas transport properties.
It is concluded that film-forming PAIs and coPAIs have a reasonably good potential as high-temperature dielectrics and membrane materials for gas separation.

Introduction

Inrtrachain 'dilution' of imide cycles with molecular swivels (like atoms of oxygen, methylene moieties, etc.) within chain repeating units of poly(amide imide)s (PAIs) renders the latter the ability to retain solubility in amidic solvents with relatively little sacrifice in thermal stability compared to conventional polyimides[1, 2] . However, as could be shown[2-4] for the PAI series of general structure $[- R_1 - R_2 - CONH - R_3 - NH -]_n$ (where R_1 is the trimellitimide cycle), both the chemical nature and the position of a swivel along the chain strongly affected the molecular mobility of PAIs. In fact, the increase in overall chain stiffness attending substitution of methylene unit by aryl ring in R_2 (i.e., replacement of the trimellitimide-N-acetic residue by the trimellitimide-N-benzoic one) resulted in the systematic increase of the glass transition temperature T_g for samples with the same diamine fragments R_3; on the other hand, for samples with the same $R_1 - R_2$ moities the increase of the relative content of molecular swivels in R_3 led to the opposite effect. The properties of thin films of PAIs depend on the pattern of chain aggregation which is believed to be genetically linked to

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the degree of interchain association in the initial solution. It is thus the purpose of this presentation to illustrate the efect of chemical composition of both dianhydride and diamine moities in the main chain of PAIs on their behavior in solution and on properties in the bulk state.

Experimental

Materials

Dichlorodianhydrides of trimellitimide- (TMA) and pyromellitimide-N-acetic acids (PMA), and of trimellitimide-N-benzoic acid (TMB) were prepared by reaction with thionyl chloride and subsequent recrystallization from the corresponding solution. Chemical grade linear aromatic diamines (LAD) and a cardo diamine (CDA), 9,9'-bis-phenylfluorene, were used as received.

Poly(amide imide)s from TMA and PMA, LAD and/or CDA (series PAI-1); a similar series (PAI-II) from TMB, LAD and/or CDA; and a series of coPAIs from TMA and mixtures of diphenylmethane diamine (DPA) with CDA were synthesized[3-5] by mixing the required quantities of the above reagents in N,N'-dimethyl acetamide (DMAA) cooled below room temperature, with subsequent vigorous stirring for 2 hr in argon atmosphere. The reaction products were precipitated with water, washed with water and acetone, and dried in vacuo at 373 K up to a constant weight

Methods

The intrinsic viscosities $[\eta]$ in DMAA at room temperature were evaluated from the standard virial equation

$$\eta_{sp} = [\eta]\, C + K_H [\eta]^2 C^2 + ..$$

where: $\eta_{sp} = \eta/\eta_0 - 1$ is the specific viscosity, η and η_0 are the solution and solvent viscosities, C is the concentration, and K_H is the Huggins constant

Weight-average molar masses $<M_W>$ were determined by light scattering in DMAA at room temperature.

Specific heat capacity (c_p) of solutions in the temperature interval 150-370 K, as well as melting heats and melting temperatures of the solvent crystalline phase (ΔH_m and T_m) were measured by the differential calorimeter with diathermal shells[6,7] at the heating rate 2 deg/min after sudden quenching of the samples in liquid nitrogen.

A similar instrument[6, 7] was used to determine the heats of dilution (ΔH_{dil}) of PAI solutions by DMAA from the initial volume content φ to the final volume content φ' at room temperature. The heat of dilution ΔH_{dil} of each coPAI solution of the initial volume content φ was determined as the arithmetic average of at least 2-3 individual measurements.

Flow behavior of freshly prepared PAI solutions in DMAA in the temperature interval 285-373 K and in the range of shear rates 0.03- 1312 s^{-1} was studied[6,7] by the Rheotest-2 viscometer (concentric cylinders geometry).

Wide-angle X-ray scattering (WAXS) patterns of thin films cast from DMAA solutions were measured[8] in the range of scattering angles 2θ = 5-40 deg with a DRON-2,0 diffractometer (copper radiation, λ = 0.154 nm; nickel filtering of the reflected beam; step-by-step scanning regime; recording of scattered radiation with a scintillation counter and digital conversion). As usual, scattering curves for all samples were normalized by thickness and X-ray absorption.

Small-angle X-ray scattering (SAXS) data were obtained[8] with a KRM-type diffractometer (Kratky collimation; primary beam intensity control with a monitoring channel; evacuation of the sample chamber) in the range of 2θ from 3' to 5 deg (copper radiation; nickel filtering of the primary beam; step-by-step scanning regime; recording of scattering radiation with a scintillation counter and digital conversion). The geometrical parameters of X-ray beam in the specimen plane and the detector position were chosen so as to satisfy the conditions of an "infinite" slit collimation (30 mm for the length of the homogeneous portion of X-ray beam and 290 mm for the specimen-detector distance).

Thermogravimetric analysis (TGA) data were obtained[9] with the Mettler Thermal Balance (nitrogen flux; temperature interval: 303-973 K; heating rate: 10 deg/min).

The complex tensile modulus (E^*) and its real and imaginary components (i.e., dynamic storage modulus E' and loss modulus E''), as well as the mechanical loss factor ($tan\ \delta$) of rectangular specimens (size 60x10 mm^2) were determined[9] with the dynamic mechanical thermoanalyzer (DMTA) (Eplexor 150 N of Gabo Qualimeter) in the load-controlled sinusoidal tensile loading regime (mean static load: 10 N; superimposed oscillating load: ± 50 N). In each experimental temperature-sweep run at one of three constant frequencies (f = 1, 10 and 100 Hz; temperature interval: 303- 703 K; heating rate: 5 deg/min) a new specimen of the same composition was used.

The isothermal dielectric behavior characterized by the complex dielectric permittivity, $\varepsilon(f) = \varepsilon'(f) - i\varepsilon''(f)$, was studied[8] with the broadband dielectric relaxation spectroscopy, DRS

(automated a.c. bridge, model HP 4182A; temperature interval: 173-573 K; frequency range: $f = 10^2$ -10^6 Hz). PAI films with silver electrodes of thickness 75 nm deposited on both sides were used for DRS measurements.

Permeabilities (P) for pure O_2, N_2, CO_2 and CH_4 gases were measured[10] (temperature: 308 K; pressure: 0.1 MPa) by the standard automated techniques based on the time-lag method. Effective gas diffusion coefficients (D) were estimated from time-lag data (upstream pressure: 0.2 MPa; temperature: 308 K) by the relation $D = l^2/6\theta$ (where θ is the time lag), and the apparent solubilities were calculated as $S = P/D$. All gases were stated by the supplier (Messer Griesheim GmbH) to be at least 99.5 % pure and were used without further purification.

Results and discussion

Properties of solutions

i) A common feature of all solutions is the unusually strong depression of both the melting heat ΔH_m (0) and the melting temperature T_m (0) of the solvent (DMAA) with polymer volume fraction φ. It is believed that strong affinity between the solvent and the polymer solute manifested itself by sterical immobilization of the molecules of the former, each of volume V_S, in molecular cavities within the latter. The mean cavity volume V_0 is assumed to be sufficiently large to incorporate several molecules of the solvent, but still smaller than the size of the critical crystallization nucleus of the latter. As a result, the reduced melting heat is expected to decrease with φ in a linear fashion as expressed by the empirical equation[11]

$$\Delta H_m/\Delta H_m\,(0) = 1 - \varphi\,(1 + \alpha)\,, \qquad (1)$$

where $\alpha = V_0/V_S > 1$. The experimental data reasonably obeyed eq. (1) ; however, one observed jump-like increases of the slope of the $\Delta H_m/\Delta H_m(0)$ vs. φ plots (from about $\alpha \cong 2$ at $\varphi < \varphi^* = 0.13$-$0.15$ to $\alpha^* \cong 2.70$ above φ^*) which were interpreted as cross-overs from the dilute solution regime to the semi-dilute solution regime at the coil overlap concentration φ^*.

The observed depression of the solvent melting temperature can be empirically accounted for by the cavity model through the classical Flory equation[12]

$$1/T_m - 1/T_m\,(0) = -\,[R/\Delta H_m\,(0)]\,[ln\,(1-\varphi) + \varphi - \chi\varphi^2] \qquad (2),$$

(where $T_m\,(0) = 258$ K is the melting point of the pure DMAA) with[11]

$$\chi = \chi_0(1 - \zeta\alpha)\,, \qquad (3)$$

where χ_0 is the classical (i.e., positive by sign and small by magnitude) parameter of polymer-solvent interactions[12], and $\zeta >> 1$ is the numerical fitting parameter.

ii) The observed decrease of negative (exothermic) heats of dilution ΔH_{dil} with φ over the entire concentration interval up to φ = 1.0 (i.e., bulk solid state) can be approximated by two straight lines with different slopes at low and high concentrations, respectively. The linearity of the steeper plot in the range of low φ means meeting the conditions of "infinite" dilution ($\varphi >> \varphi'$) and $\chi n_2 x \approx const$ or all studied coPAIs, whereas its large negative slope can be explained by large negative values of χ implying strong affinity between coPAIs and DMAA, in the equation[4, 5]

$$\Delta H_{dil} = RT\chi x n_2 (\varphi - \varphi'), \qquad (4)$$

(where n_2 is the number of polymer molecules, and x is the degree of polymerization).

The linearity of the ΔH_{dil} vs. φ plots at higher φ suggests that the structure of all samples in this concentration interval is the same as that of the corresponding bulk solid. As proved by X-ray scattering studies[2, 8], all PAIs in the bulk state are amorphous (glassy) solids; hence, the major part of the observed negative heats of their dissolution in DMAA, ΔH_{dis}, should be attributed to the release of the excess enthalpy of the metastable glass relative to the corresponding equilibrium melt, as expressed by the following equation[13, 14]:

$$\Delta H_{dis} \approx <\Delta c_p> (T - T_g), \qquad (5)$$

where $<\Delta c_p>$ is the mean difference between specific heat capacities of the metastable glass and of the hypothetical equilibrium melt in the interval between the temperature of measurements T (= 295 K) and the glass transition temperature T_g.

iii) The "shear thickening" phenomenon (i.e., the increase of the apparent viscosity η with shear rate γ) preceding the expected "normal" shear thinning effect was observed[6] for semi-dilute solutions of symmetric PAI (TMI/LAD) at $\varphi > \varphi^*$. The cross-over from shear-thickening to shear-thinning flow behavior with increasing γ was explained by the initial shear-induced lateral association of chain segments into large-size flow units ("clusters") followed by subsequent breakdown of the latter above the critical shear rate γ^* (corresponding to maxima on the *log* η vs. *log* γ plots). The absence of this effect for solutions of strongly asymmetric cardo PAIs was explained by a significantly higher degree of interchain association due to the strong electron donor/acceptor interactions already in the quiescent state. The degree of intersegment interactions of coPAIs increased, and the contribution of shear-thickening flow mechanism of semi-dilute solutions decreased, the lower the DPA/CDA ratio[7].

The apparent dilute solution/semi-dilute solution regime cross-overs at fairly low φ^* also manifested themselves as discontinuous, jump-like changes of the apparent activation energies for viscous flow[6,7].

Solid state properties

i) The presence of broad diffuse maxima on the WAXS patterns of all PAIs and coPAIs is the experimental evidence for their non-crystalline (glassy) state[8, 9]; however, the asymmetricity of the profiles of essentially amorphous halos is indicative of a weak para-crystalline order (presumably, due to a lateral aggregation of self-associated chain fragments). The mean interchain distances $<d_1>$, as well as effective chain stiffness (characterized by the mean persistence length $<p>$) tended to increase with the CDA/DPA ratio[9]. The smooth patterns of the SAXS curves suggest the absence of large-scale structural heterogeneities in all samples; however, in view of the WAXS data this can be explained by the smearing-out of electron density differences between densely-packed and loosely-packed microregions of coPAIs due to a wide dispersion of their sizes[8,9].

ii) The four step-like weight losses on the TGA traces were interpreted as follows [9]. The smaller weight losses Δm_1 and Δm_2 around $T_1 \cong 350$ and $T_2 \cong 540$ K most probably, are related to the successive evaporation of traces of moisture and of DMAA which were trapped into coPAIs during the film casting procedure. Carbonyl groups within dianhydride fragments of PAI chains are the most probable sites to interact with water molecules through hydrogen bonds, whereas electron donor-acceptor interactions can be expected between DMAA molecules and the arylene units of coPAIs. Comparing the experimental values of Δm_1 and Δm_2 with the theoretical estimates, it can be concluded that it is only each third/fourth carbonyl group and arylene unit within chain repeating units of coPAIs which is involved in specific interactions with molecules of water and of DMAA, respectively. Assuming that the potentially active sites in the densely-packed regions are inaccesible for such interactions, it follows from the above estimates that the loosely-packed regions comprise about 25-35 % of the total volume of studied coPAIs.

The two larger weight loss stages 3 and 4 in the temperature interval above 600 K involve successive degradation of different moieties within the chain repeating units of coPAIs (presumably, diamine and dianhydride fragments, respectively). The characteristic feature of TGA data for all studied PAIs is that the weight loss process is far from complete by the end

of the final stage 4 at T = 973 K; in fact, the cumulative weight loss $\Delta m_3 + \Delta m_4$ for all samples does not exceed 35-40 %.

iii) Common to the DMTA data for all studied PAIs and coPAIs was the occurrence of the following three distinct temperature intervals with radically different patterns of $log\ E^*$ vs. T dependence[9]:

1. The initial smooth decrease in the solid (glassy) state;

2. The step-like drop by more that three orders of magnitude accompanying the transition into rubbery state;

3. The final steep increase (presumably, due to a cross-linking concomitant to the onset of oxidative degradation).

4. In the second temperature interval, one can observe two sub-intervals of the steep $log\ E^*$ decrease at lower and upper temperature bounds (which correspond to the low-temperature shoulders around $T_{\alpha'}$ and to the high-temperature peaks at T_α, respectively, on the $tan\ \delta$ vs. T plots) separated by a broad intermediate sub-interval. Judging by the high values of the apparent activation energies, $\Delta E_{\alpha'}$ and ΔE_α, calculated from the frequency dependencies of $T_{\alpha'}$ and T_α, the sudden drops of $log\ E^*$ in these latter temperature sub-intervals can be attributed to the cooperative segment motion of PAI chains in loosely-packed and in densely-packed regions, respectively

The glass transition temperatures of all studied PAIs (identified as T_α on the DMTA plots) tended to increase linearly with the apparent volume of the relevant kinetic unit (i.e., the product of chain persistence length $<p>$ by chain cross-sectional area $<d_l>^2$) from about 540 K for PAI (TMA/DPA) to 625 K for PAI (PMA/CDA).

iv) Nearly all (carefully outgassed) samples of PAIs exhibited a smooth increase of the dielectric permittivity ε' (from about 4 at 173 K to 6 at 573 K) concomitant with the occurrence of distinct low-temperature peaks (γ–relaxation), of broad maxima at intermediate temperatures (presumably, overlapping β- and α'–relaxations), and of final upswings on the approach to glass transition regions (i.e., the onset of conductivity) in the dielectric loss factor ε'' vs. T curves[8]. Judging by such a relatively small (by a factor of only 1.5) change of ε' in the temperature span of almost 400 K, the majority of studied PAIs may have a potential as high-temperature dielectrics.

v) The permeability P to gases[10] increased with the free volume fraction-controlled diffusion coefficient D and was higher for PAI (TMA/CDA) compared to PAI (TMA/LAD). The solubilities S of PAI (TMA) correlated with the molar cohesion energy density. Fluorination

of the central aryl unit in the PAI (TMA/HEA) resulted in the increased diffusion and solubility coefficients, while the highest values of these parameters were observed for PAI (PMA/CDA). The total permeation selectivity was dominated by solubility contribution. The temperature dependencies of *P, D* and *S* could be accounted for by Arrhenius and van't Hoff equations, respectively.

Judging by the reasonably high permeation selectivities [e.g., P (CO_2)/P (CH_4) > 90], PAI (TMA/TFA) and PAI (TMA/CDA) may have a good potential as gas separating membranes[10].

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