

Synthesis of poly((2-dimethylamino)ethyl methacrylate) via atom transfer radical polymerization and surface characterization by inverse gas chromatography

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Poly(2-dimethylamino)ethyl methacrylate) (PDMAEMA) was synthesized via atom transfer radical polymerization. The synthesized PDMAEMA was characterized by FTIR, GPC and DSC. The inverse gas chromatography technique was used to obtain the surface properties of PDMAEMA. The retentions of nonpolar solvents such as n-hexane, n-heptane, n-octane, n-nonane, n-decane and other acidic, basic and amphoteric probes such as tetrahydrofuran, dichloromethane, chloroform, acetone, ethyl acetate and benzene used without further purification on PDMAEMA were measured in the temperature ranges from 303 to 373 K by inverse gas chromatography (IGC). The dispersive component of the surface energy, γ_S^D of studied adsorbent surface was estimated using retention times of different nonpolar organics in the infinite dilution region. Dispersive components of the surface energies, γ_S^D according to Fowkes and Dorris-Gray approaches and the acid, K_A and base, K_D constants for PDMAEMA were calculated.

Keywords: Poly(2-dimethylamino)ethyl methacrylate); Inverse gas chromatography; Surface and adsorption properties; Surface free energies; Lewis acid-base constants

INTRODUCTION

Poly[2-(dimethylamino)ethyl methacrylate] has attracted a significant attention in recent years as a cationic pH and temperature responsive polymer for an increasing number of applications in drug delivery, bioseparation, and microfluidic areas. [1] The inverse gas chromatography(IGC) method which is simple, fast, economical method has been used extensively to study the structure of polymers, the interactions of various liquids and gases with polymers and to provide valuable thermodynamic information for surface characterization of polymeric substances [2-4].

In this study, poly(2-dimethylamino)ethyl methacrylate) (PDMAEMA) which was synthesized via atom transfer radical polymerization using CuBr ligated with N,N,N',N',N''-pentamethyl-diethylenetriamine (PMDETA) as catalyst, and ethyl 2-bromoisobutyrate (EBiB) as initiator under argon atmosphere. The synthesized PDMAEMA was characterized by FTIR, GPC and DSC. The inverse gas chromatography technique was used to obtain the surface properties of PDMAEMA.

EXPERIMENTAL PART

Probes and Instrumentation

The used solvents were high purity grade nonpolar solvents such as n-hexane (Hx), n-heptane (Hp), n-octane (O), n-nonane (N), n-Decane (D) and polar solvents such as dichloromethane (DCM, acidic), chloroform (TCM, acidic), acetone (Ac, amphoteric), ethyl acetate (EA, amphoteric), tetrahydrofuran (THF, basic) and benzene. The all studied solvents and support materials being Chromosorb-W(AW-DMCS-treated, 80/100 mesh) were supplied from Merck AG. Inc. Silane treated glass wool used to plug the ends of the column was obtained from Alltech Associates, Inc.,

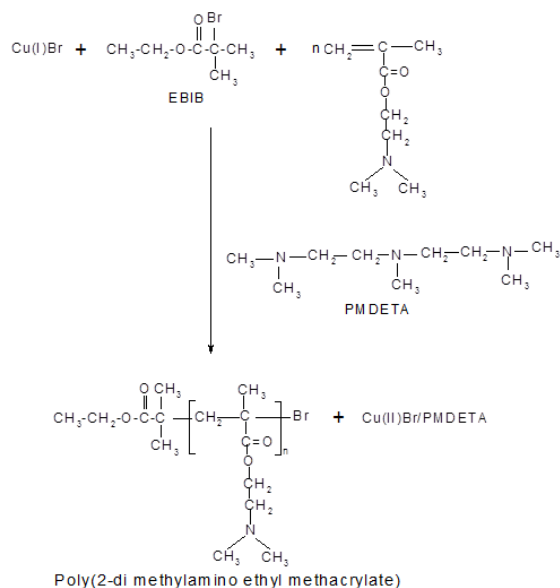
PDMAEMA was used as a stationary phase in the chromatographic column and solvents with a different chemical nature were used as eluents. The retention diagrams of studied solvents on PDMAEMA were plotted at temperatures in K between 303 and 373 by IGC. The sorption properties of the PDMAEMA were determined using a Hewlett-Packard 6890 Series II gas chromatograph, with a thermal conductivity detector (TCD). High purity helium was used as the carrier gas (flow rate in the range 25–28 cm³ min⁻¹). A stainless steel columns (0.5 m long, 3.2 mm o.d.) were packed with PDMAEMA covered on chromosorb. After packing, the columns were conditioned overnight at 373 K. The retention diagrams of studied solvents on PDMAEMA were

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plotted at temperatures in K between 303 and 373 by IGC.

Synthesis of poly((2-dimethylamino)ethyl methacrylate) via atom transfer radical polymerization

Poly(2-dimethylamino)ethyl methacrylate) (PDMAEMA) which was synthesized in Schlenk tube via atom transfer radical polymerization of 2-dimethylamino ethyl methacrylate (7.5 ml) using CuBr (0.039 gr, 0.27 mmol) ligated with N,N,N',N',N''-pentamethyl-diethylenetriamine (0.15 ml, [PMDETA]=0.0466 M, $M_w=173.3$ g/mol, $d=0.83$ gr/cm³; PMDETA) as catalyst, and ethyl 2-bromoisobutyrate (1.32 ml, $M_w=195.06$ g/mol, $d=1.329$ gr/cm; EBiB) as initiator under argon atmosphere in dichloromethane and one day at room temperature. After 24 h, it was observed heterogen phase. Green part of solution was diluted with DCM, heterogen phase was filtered and precipitated in cool n-heptane. Waxy green-blue precipitate was passed on basic alumina for purification. Solution was precipitated in n-hexane and synthesized polymer was characterized by FT-IR, GC and DSC. (Scheme 1)



Scheme 1. Synthetic Route of Poly((2-dimethylamino)ethyl Methacrylate) via Atom Transfer Radical Polymerization

THEORY OF INVERSE GAS CHROMATOGRAPHY

The surface polarity and the acid-base nature of materials can be measured by IGC technique. This technique supplies a basis for determining the potential for chemical interaction between the polymer and solvent. The investigated material is immobilised within a chromatographic column

which is flushed through with inert gas such as helium or nitrogen. The stationary phase characterisation is achieved by utilising the partitioning of the sample between the mobile phase and the stationary phase, indicated by the time taken to elute the sample. The probe-probe interactions in IGC experiments are negligible because of carried out in infinite dilution. The theory and the technique are now quite well described in literature [5-6].

The dispersive component of surface energy, γ_s^D were determined by Dorris-Gray and Fowkes approaches. The adsorption energy for the non-polar solvents increases with the number of carbon atoms in the chain.

According to Dorris and Gray approach, the increment, corresponding to the adsorption energy of a methylene group, $\Delta G_{A[CH_2]}$ is given by [7]

$$\Delta G_{A[CH_2]} = -RT \ln \left(\frac{V_{N,n}}{V_{N,n+1}} \right), \quad (1)$$

where $V_{N,n}$ and $V_{N,n+1}$ are the retention volumes of two n-alkanes having n and n+1 carbon atoms in their chain. This parameter is independent of the chosen state of the adsorbed molecule. Thus at constant temperature, for a series of alkane probes, a plot $RT \ln V_N$ versus the number of carbon atoms should give a straight line from which $\Delta G_{A[CH_2]}$ can be found.

The methylene adsorption energy can also be defined as [7]

$$\Delta G_{A[CH_2]} = 2N_A a[CH_2] \sqrt{\gamma_s^D \gamma_L[CH_2]}, \quad (2)$$

where N_A is Avagadro's number, $a[CH_2]$ is the surface area covered by one methylene group (0.06 nm²) and $\gamma_L[CH_2]$ is the surface free energy of a surface consisting of methylene groups, i.e. polyethylene, given by

$$\gamma_L[CH_2] = 35.6 + 0.058(293 - T), \quad (3)$$

Thus using Eqs.(1)-(3) and the experimentally determined values of the adsorbate net retention volumes, $V_{N,n}$ and $V_{N,n+1}$, the dispersion component of the surface free energy, γ_s^D may be calculated and where the adsorbate net retention volumes, V_N were calculated from the expression:

$$V_N = Q * J * (t_R - t_A) * T / (T_f), \quad (4)$$

In equation (1), t_R is the adsorbate retention time, t_A is the retention time of air, Q is volumetric flow rate measured at column outlet and

at ambient temperature T_f (K), T is the column temperature (K) and J is James-Martin gas compressibility correction factor [8].

According to the Fowkes approach, the dispersive component of surface energy, γ_s^D is calculated following equation [9]:

$$-\Delta G_A = RT \ln(V_n) = 2Na(\gamma_s^D)^{0.5}(\gamma_L^D)^{0.5} + K'' \quad (5)$$

Thus for a series of n-alkane probes, a plot of $RT \ln V_N$ against $a(\gamma_L^D)^{0.5}$ will give a slope of $2N(\gamma_s^D)^{0.5}$. Values of $a(\gamma_L^D)^{0.5}$ and boiling point, T_b ($^{\circ}C$) of apolar solvents are found in the literature [10-11].

The specific component of the free energy is determined from the n-alkane plot of $RT \ln V_N$ against $a(\gamma_L^D)^{0.5}$. The distance between the ordinate values of the polar probe datum point and the n-alkane reference line gives the specific component of the surface free energy, $-\Delta G_A^S$.

An equation may be written for this procedure,

$$-\Delta G_A^S = RT \ln\left(\frac{V_{N,n}}{V_{N,ref}}\right) \quad (6)$$

where $V_{N,n}$ and $V_{N,ref}$ are the retention volume for the polar probe and the retention volume for the n-alkanes' reference line, respectively.

The adsorption of a polar probe onto the adsorbant surface leads to a change in the enthalpy of the system and the entropy of the system. These factors are related to the energy of adsorption by the equation,

$$\Delta G_A^S = \Delta H_A^S - T\Delta S_A^S \quad (7)$$

Here, ΔH_A^S is the adsorption enthalpy by Lewis acid-base interactions, ΔS_A^S is the adsorption entropy Lewis acid-base interactions and T is the column temperature. For each polar probe, ΔH_A^S and ΔS_A^S can be determined from a plot of $-\Delta G_A^S/T$ against $1/T$.

The surface Lewis acidity and basicity constants, K_A and K_D , may be calculated from the equation,

$$-\Delta H_A^S = K_A DN + K_D AN^* \quad (8)$$

Here, DN and AN^* are Gutmann's donor and modified acceptor numbers, respectively. Values of $a(\gamma_L^D)^{0.5}$ and boiling point, T_b ($^{\circ}C$) of non-polar solvents are found in the literature [12,13] and the Gutmann's modified acceptor number, AN^* and

donor number, DN of the polar probes used in this study are found in the literature [14,15].

K_A and K_D are obtained from a plot of $-\Delta H_A^S/AN^*$ versus DN/AN^* with K_A as the slope and K_D as the intercept. Parameters K_A and K_D reflect the ability of the examined surface to act as an electron acceptor and electron donor, respectively [12,13].

RESULTS AND DISCUSSION

Characterization of poly((2-dimethylamino)ethyl methacrylate)

The yield of synthesized PDMAEMA via ATRP was calculated about 50%, Mn= 3500 g/mol from GPC, PDI=1.1, very low T_g and structural characterized by FTIR/ATR (Fig.1).

According to FTIR/ATR spectrum of PDMAEMA; 2770-2952 cm^{-1} aliphatic C-H, 1725 cm^{-1} de ester C=O, 1456 cm^{-1} aliphatic C-H, 1149 and 1270 cm^{-1} C-O-C asymmetric and symmetric, 1059 cm^{-1} C-N, 749 cm^{-1} aliphatic C-H.

Surface properties of poly((2-dimethylamino)ethyl methacrylate)

The net retention volumes, V_N of studied solvents on PDMAEMA were calculated from igc measurements at infinite dilution region using Eq (1). The retention diagrams of studied solvents on PDMAEMA were plotted at temperatures between 303 and 373 K and given Figure 2 (a) for nonpolar and Figure 2(b) for polar solvents.

The slope of the fitted line is equal to $\Delta G_{A[CH_2]}$.

The variation of γ_s^D and $\gamma_L[CH_2]$ with temperature were calculated from Eq.(3) and (4), respectively. The adsorption energy of a methylene group, $\gamma_L[CH_2]$ the surface free energy of a surface consisting of methylene groups, $\Delta G_{A[CH_2]}$ and dispersion component of surface free energy, γ_s^D values calculated by Doris-Gray approach for PDMAEMA determined at studied temperatures and the results were given in Table 1.

The Fowkes equation (Eq. 5, referred to as Schultz and Lavielle approach by some authors) [16] was used to determine the dispersive component of the surface free energy, γ_s^D over a range of studied temperatures and calculated values of $RT \ln V_N$ were plotted against $a(\gamma_L^D)^{0.5}$. An example of the pattern of results obtained was given in Fig. 4 for the isotherm at 303 K.

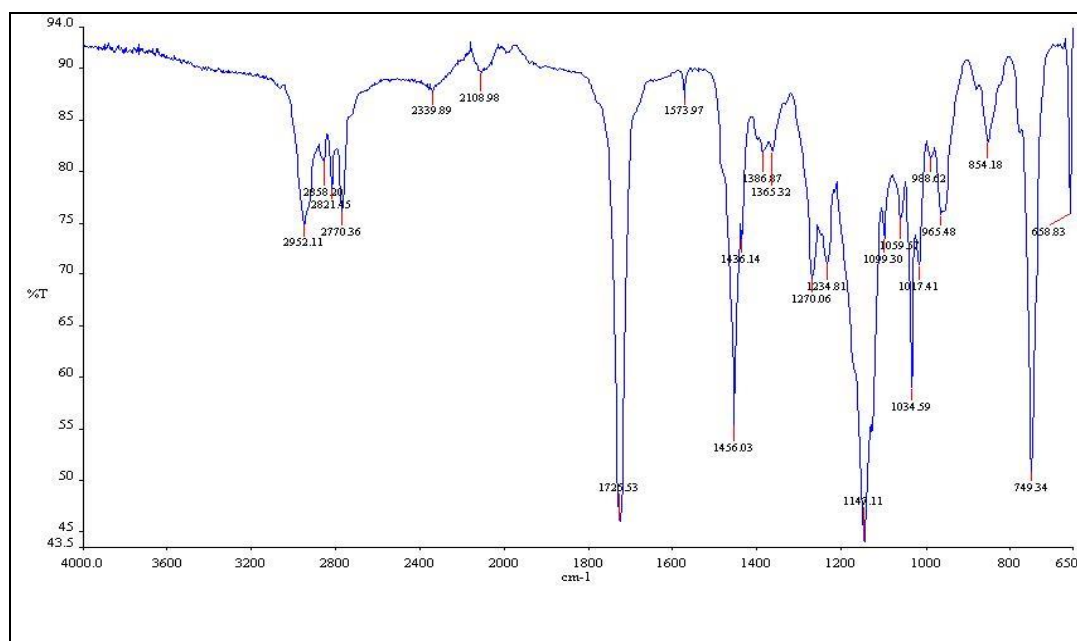


Fig. 1. FTIR/ATR spectrum of PDMAEMA

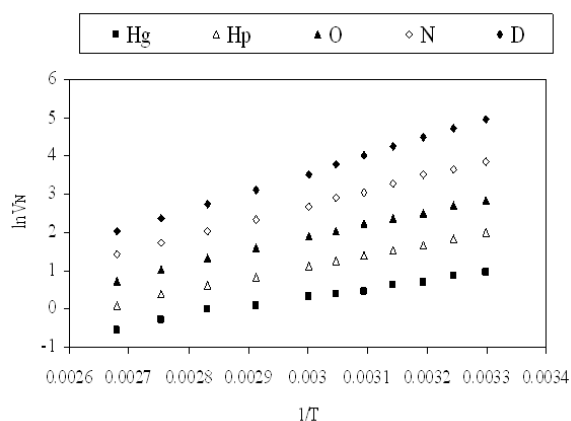


Fig. 2 (a). The retention diagram of non-polar solvents adsorbed onto PDMAEMA

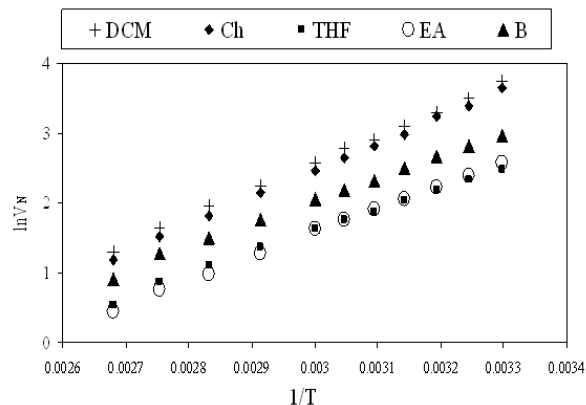


Fig. 2 (b). The retention diagram of polar solvents adsorbed onto PDMAEMA

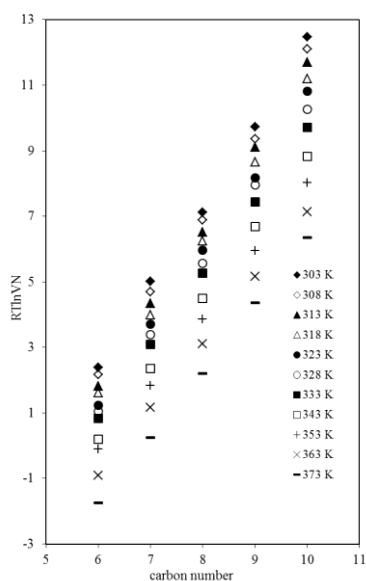


Fig 3. The plot of $RT \ln V_N$ versus carbon number of non-polar solvents for PDMAEMA

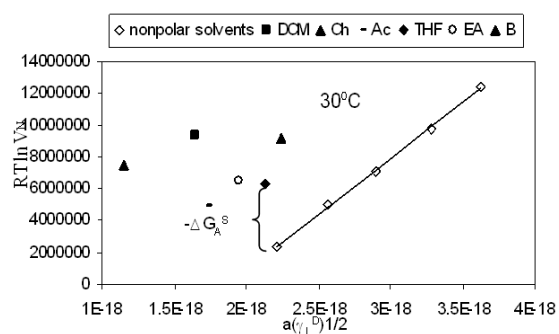


Fig. 4. Variation of the logarithm of the retention volume of non-polar and polar versus solvents $D 0.5 a(\gamma_L) [m^2(mJ/m^2)^{0.5}]$ at 303 K

According to Dorris-Gray approaches, Eq.(2), $\Delta G_{A[CH_2]}$ is independent of the chosen reference state of adsorbed molecule. The $RT \ln V_N$ versus carbon number of non-polar solvents were plotted in Fig.(3) for PDMAEMA. The results of

$\Delta G_{A[CH_2]}$, $\gamma_L[CH_2]$ and γ_S^D of PDMAEMA was given in Table 1.

The linearity was obtained by the non-polar solvents at the studied temperature ranges. The slope ($2N\sqrt{\gamma_S^D}$) of the linear fit, obtained for each non-polar solvent plot, gives the dispersive component of the surface free energy, γ_S^D at that temperature.

The γ_S^D values of PDMAEMA calculated according to Fowkes approach at studied temperature ranges were given in Table 1.

Table 1 report that the variation of γ_S^D as a function of temperature was limited and the γ_S^D values of PDMAEMA decrease significantly between 303 and 373 K.

The values of γ_S^D of PDMAEMA calculated according to Dorris-Gray and Fowkes approaches are very close to each other at the studied temperature ranges. There is no data in the literature to compare these values. The specific component of the surface free energy, ΔG_A^S , is calculated using the difference between the calculated value of $RT \ln V_N$ and that which was derived using the equation of the linear fit of the n-alkane reference line (Eq.7).

ΔH_A^S and ΔS_A^S can be determined from a plot of $-\Delta G_A^S/T$ against $1/T$. (Eq.8)

Table 1. The adsorption energy of a methylene group, $\gamma_L[CH_2]$ the surface free energy of a surface consisting of methylene groups, $\Delta G_{A[CH_2]}$ and dispersion component of surface free energy, γ_S^D values of PDMAEMA calculated by Doris-Gray (D-G) and Fowkes (F) approaches and slope at studied temperatures for PDMAEMA

T(K)	$\gamma_L[CH_2]$ (mJ/m ²)	$\Delta G_{A[CH_2]}$ (10 ⁶ mJ/mol)	γ_S^D (D-G) (mJ/m ²)	Slope (x10 ²⁴)	γ_S^D (F) (mJ/m ²)
303	35.02	2.49	33.87	6.993	33.73
308	34.73	2.45	33.19	6.893	32.78
313	34.44	2.45	33.46	6.894	32.79
318	34.15	2.38	31.88	6.699	30.96
323	33.86	2.36	31.58	6.636	30.38
328	33.57	2.30	30.23	6.468	28.86
333	33.28	2.21	28.08	6.204	26.55
343	32.7	2.16	27.32	6.067	25.39
353	30.96	2.03	25.50	5.721	22.58
363	32.12	2.04	24.73	5.706	22.46
373	31.54	2.01	24.54	5.648	22.01

The values of K_A and K_D were calculated using Eq.(9). The plotting $-\Delta H_A^S/AN^*$ versus DN/AN^* with K_A as the slope and K_D as the intercept. The plot of $-\Delta H_A^S/AN^*$ versus DN/AN^* for PDMAEMA was given at Fig.5.

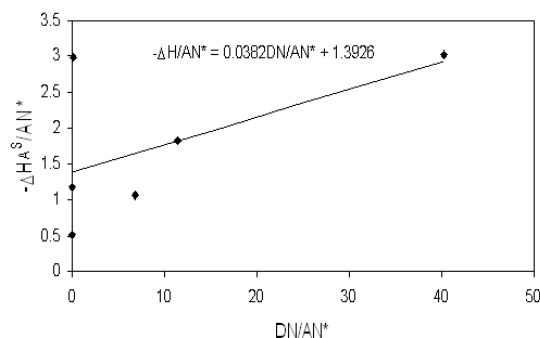


Fig. 5. The plot of $-\Delta H_A^S/AN^*$ versus DN/AN^* for PDMAEMA.

The values of K_A and K_D are found to be 0.04 and 1.4 for PDMAEMA and the values If the ratio of K_D to K_A is greater than 1, solid surface is basic nature and below 1, it implies that the solid surface is acidic nature [17]. According to the K_D/K_A ratio of PDMAEMA, it is found that the surface of PDMAEMA has basic nature.

CONCLUSIONS

Adsorption properties, surface and Lewis acid-base characteristics of PDMAEMA synthesized successfully via atom transfer polymerization have been examined by means of inverse gas chromatography at infinite dilution, in the temperature range from 303 to 373 K. The γ_s^D values of PDMAEMA change ranges from 33.87 to 24.54 mJ/m² (Dorris-Gray approach) and from 33.73 to 22.1 mJ/m² (Fowkes approach) with increasing temperature. The values of K_A and K_D parameters indicated that PDMAEMA surface is basic nature. IGC is a convenient method for the characterization of the surface and adsorption properties and the acid-base characteristics of acrylate derivatives.

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