Porous terpolymers: poly(acrylonitrile-*co*-ethyl/butyl/acrylate-*co*-divinylbenzene)

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A series of terpolymers was prepared from acrylonitrile, ethyl or butyl acrylate and divinylbenzene (10 wt %). The terpolymers were obtained by suspension polymerization with inert diluents. They had a porous structure unless the amount of acrylate exceeded 50 mol %. The porous structure, however, was not permanent. By heating the copolymers above T_g or treating with solvents, a porosity as high as 40 % could be made to disappear. The inverse gas chromatography (i.g.c.) measurements revealed that the segmental motion of terpolymer chains appeared in the temperature ranges where the segmental mobility of poly(acrylonitrile) is observed (~95, 120–160°C). It may be concluded from the values of Kovats indices that the hydrophilicity of the surface area of terpolymers is higher than that of acrylonitrile–divinylbenzene copolymers.

(Keywords: terpolymers; poly(acrylonitrile-*co*-ethyl/butyl/acrylate-*co*-divinylbenzene); porous structure; i.g.c.)

INTRODUCTION

Crosslinked porous copolymers of acrylonitrile (AN) and divinylbenzene (DVB) and terpolymers of acrylonitrile, ethyl (EA) or butyl (BA) acrylate and DVB are interesting products that are used as sorbents[1,2] and stationary phases of gas chromatography[3]. Chemical modification of these products with amines led to a group of specific sorbents[4], anion-exchange resins[5] and carriers for biologically active substances[6–8].

The properties of suspension terpolymers poly(acrylonitrile-*co*-ethyl or butyl acrylate-*co*-divinylbenzene), PANE, PANB, of small cross-linking degree have not been yet described. In the patent literature, there is some data on the synthesis and modification of acrylate–DVB copolymers[8,9] or on the synthesis of vinyl copolymers including AN, acrylate and DVB[10,11].

It is known that aliphatic acrylates facilitate segmental motions of chains of vinyl polymers. Copolymers of AN and acrylates were expected to have a less ordered structure and weaker intermolecular interactions than polyacrylonitrile alone[12–17].

In this work, the effect of the presence of acrylate units (EA or BA) upon the surface properties and segmental mobility in porous terpolymers (PANE and PANB) is investigated.

EXPERIMENTAL

The terpolymers were synthesized in suspension in conditions described elsewhere[1,2]. The compositions of monomer feeds are listed in *Table 1*.

The polymers were extracted with hot benzene, treated with acetone and water and stored wet. The dry mass was determined after drying the samples at room temperature to constant weight. The porous structure was characterized as described in reference 2.

The sorbents of medium particle size (0.1–0.05 mm) were packed into 1 m glass columns ($\phi = 0.8$ mm) and heated in a constant stream of nitrogen. The temperature was raised from 100 to 200°C over a period of 10 h.

The i.g.c. measurements were made on a Perkin–Elmer F-11 chromatograph equipped with FID. Samples of n-alkanes (0.2 μl) were injected at 150°C. Similar samples of n-alcohols were injected at 70–160°C. The nitrogen rate was 25 ml min^{-1}. Each retention time, τ_R, was an average from five measurements.

RESULTS AND DISCUSSION

Copolymers of AN and DVB obtained in the presence of inert diluents readily form porous structures because of the additional crosslinking with strong intermolecular interactions. These interactions, on the other hand, cause difficulties in the chemical modification of polymers. An introduction of EA or BA units into the suspension polymerization system was aimed at the internal plasticization of the copolymers.

The properties of terpolymers with varying amounts of acrylate units are presented in *Tables 1* and *2*. The porosities of PANB terpolymers remain constant up to 20 mol % of acrylate units. The terpolymers containing up to 48 mol % BA or 55 mol % EA units still have porous structures (*Figure 1*) although the pore volume gets smaller and smaller. The terpolymers with an acrylate content exceeding these values have a so-called 'expanded structure' and their porosity may change upon treatment in broad ranges, certain styrene–DVB copolymers[18–20] have a similar structure.

The treatment leading to porosity reduction consists of exchanging a bad solvent for a better one followed by drying at room temperature, chemical modification with

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Table 1 Temperatures at which molecular motions of copolymer segments were observed

			Nitrogen content (%)		Molecular motions (°C)	
PANB/E	Monomers	Molar ratio	Calculated	Found	Rotational oscillation	Collective
I	AN	100	21.1	13.7	90–95	122–125
II	AN:BA	89:11	16.6	15.6	75–80	105, 125
III	AN:BA	80:20	13.7	11.1	70–75	125
IV	AN:BA	68:32	9.6	7.7	70	125
V	AN:BA	52:48	6.6	6.3	–	–
VI	BA	100	0	0	–	–
VII	AN:EA	72:28	10.0	8.0	80	122–125

DVB content 10 wt%
AN, acrylonitrile; BA, butyl acrylate; EA, ethyl acrylate

Table 2 Characteristics of polymers

PANB/E	I	II	III	IV	V	VI	VII
Apparent density ($g\,cm^{-3}$)	0.51	0.49	0.56	0.68	1.05	1.06	0.60
True density ($g\,cm^{-3}$)	1.18	1.16	1.15	1.13	1.10	1.14	1.17
Porosity (%)	56.7	57.5	51.3	39.8	4.9	7.0	48.4
Macroporosity ($cm^3\,g^{-1}$)	1.08	1.17	0.92	0.58	0.05	0.06	0.80
Volume of pores (%)							
micro	1.0	3.0	0.0	0.0	0.0	0.5	0.0
meso	12	25	6	4	100	95	3
macro	87	72	94	96	0.0	4.5	97
Surface area ($m^2\,g^{-1}$)	40	54	15	12	30	–	10
Water regain ($g\,g^{-1}$)	0.87	1.50	1.45	1.43	0.50	0.05	1.60
Volume fraction of polymer in gel, v_2	–	0.86	0.77	0.64	0.71	0.99	0.65

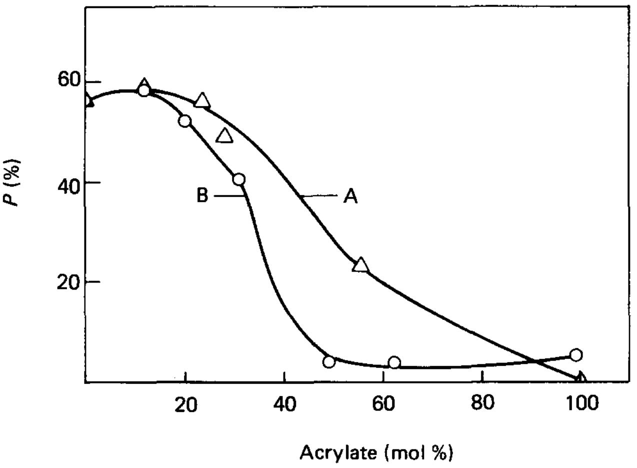

Figure 1 Porosity variation, *P*, as a function of acrylonitrile in copolymers: A, PANE; B, PANB

amines, or heating the polymers well above T_g. Terpolymer PANB-IV is a good example. Its porosity depends on the quality of solvent in which the terpolymer was swollen before drying out (*Table 3*).

From the analysis of reactivity ratios of comonomers, AN and DVB, as determined by Schwachula[21], one can expect that at the initial stage of copolymerization the copolymer is enriched in DVB. The resulting macromolecules become the precursors of microgels[2].

It is expected from the values of *Q* and *e* from the Alfrey–Price scheme[22–24] that in the terpolymer some of the acrylonitrile units of an AN/DVB copolymer are merely replaced by BA units, since the AN/BA pair forms nearly an azeotropic copolymer (*Table 4*).

Table 3 Variation of porosity of terpolymer PANB-IV after treating with diluents

Diluent	δ ($MPa^{1/2}$)	Apparent density ($g\,cm^{-3}$)	Porosity (%)
Heptane	15.1	0.875	22.6
Carbon tetrachloride	17.6	1.07	5.4
Isobutanol	21.5	1.07	5.4
Dimethylformamide	24.8	1.08	4.2
Water	47.9	0.69	39.0
Water[a]	47.9	1.09	4.0

True density, $d = 1.13\,g\,cm^{-3}$
After heating 24 h in N_2 at 210°C

Table 4 Copolymerization ratios calculated from the Q–e scheme[22–24]

Monomer 1	Monomer 2	r_1	r_2	$r_1 r_2$
AN	EA	0.356	1.075	0.38
AN	BA	1.01	0.97	0.98
AN	*m*-DVB	0.0057	0.039	2×10^{-4}
AN	*p*-DVB	2.9×10^{-4}	6.5×10^{-3}	1.9×10^{-6}
EA	*m*-DVB	0.1	9.5	0.95
EA	*p*-DVB	0.01	0.08	8.9×10^{-4}
BA	*m*-DVB	0.008	0.006	4.9×10^{-4}
BA	*p*-DVB	4.7×10^{-4}	0.01	5.1×10^{-6}

The introduction of BA units, however, changes the solvating conditions of polymerization drastically. This is because this monomer, unlike AN, is a solvent for the polymer being formed.

The effect of EA is different. By analysis of the copolymerization reactivity ratios calculated from the *Q*–*e* scheme (*Table 4*) one can conclude that EA units will be incorporated into microgel precursors and a slightly more compositionally uniform terpolymer will be formed than that with BA.

The structure of AN homo- and copolymers is still the subject of controversy[12–17]. It is well established that polyacrylonitrile forms a complex system of amorphous and paracrystalline domains[13]. The structure is usually described in terms of a one-phase model or a two-phase model with a pseudocrystalline ordered and amorphous disoriented phase[16]. Regardless of which model is accepted, it is well known that the formation of a supermolecular structure of polyacrylonitrile is strongly influenced by dipole–dipole interactions.

Two temperature ranges can be distinguished when thermal properties of polyacrylonitrile are considered. The first, at about 95°C, is attributed to thermally induced rotational oscillations. In the range 120–140, 160°C, segmental motions are observed attributed to the co-operative mobility typical of the glass transition of longer fragments of macromolecules[12].

The data published for copolymers of AN and methyl methacrylate and for AN and methacrylonitrile do not indicate great differences between the structure of copolymers and that of AN homopolymer, as revealed by wide-angle X-ray scattering measurements. Here, however, the chemical differences between units was not too great[16].

In copolymers of AN and 2-hydroxyethyl acrylate, segmental motions appeared at a lower temperature than that for polyacrylonitrile when the amount of the second comonomer was small. The situation was reversed at the higher content of 2-hydroxyethyl acrylate[15]. This was attributed to the steric conditions preventing fragments of chain from interacting with each other.

In copolymers of AN with DVB, one would expect much less ordering than in polyacrylonitrile as well as reduction of segmental motions in amorphous regions because of crosslinking. The introduction of acrylate units, on the other hand, should lead to the plasticization of terpolymer segments. The effect of the concentration of BA units upon the appearance of segmental motions in paracrystalline regions and of the collective motions, T_g for the present copolymers and terpolymers is presented in *Table 1*.

The values were deduced from retention diagrams of n-alcohols for the copolymers and terpolymers.

It is well known that as the temperature increases, the interactions change their character because of passing from the region of sorbate adsorption to the absorption region. In the retention diagram, the deviation from linearity beyond the limit of confidence is identified with T_g. At a constant flow rate of carrier gas and the same particle size of copolymers, the width of the non-equilibrium region in the retention diagram depends mainly on the kind of sorbate and on the supermolecular structure of the copolymer used to fill the columns.

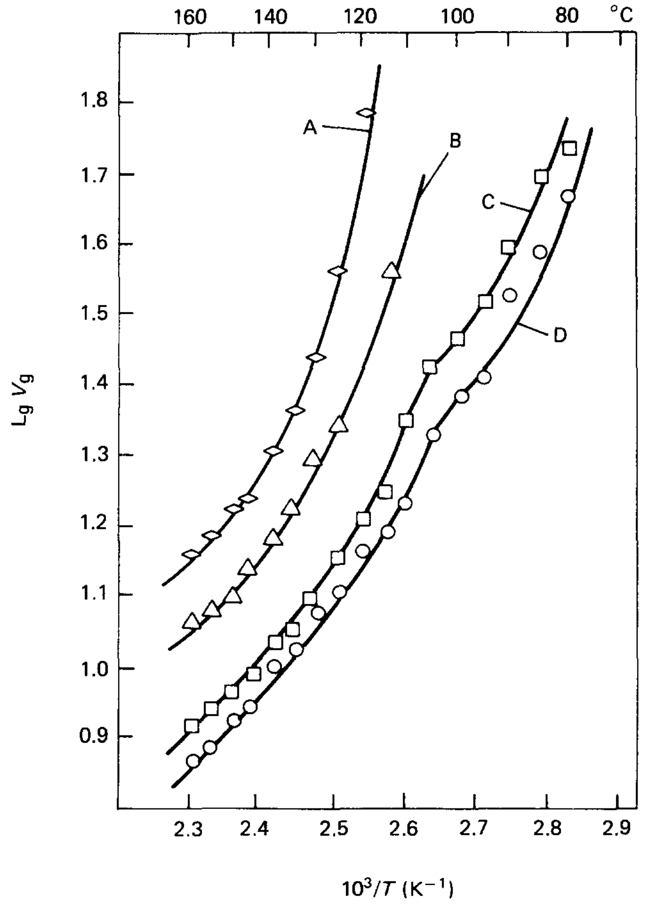

Figure 2 Retention diagrams for copolymer PAN-I. A, butanol; B, propanol; C, ethanol; D, methanol

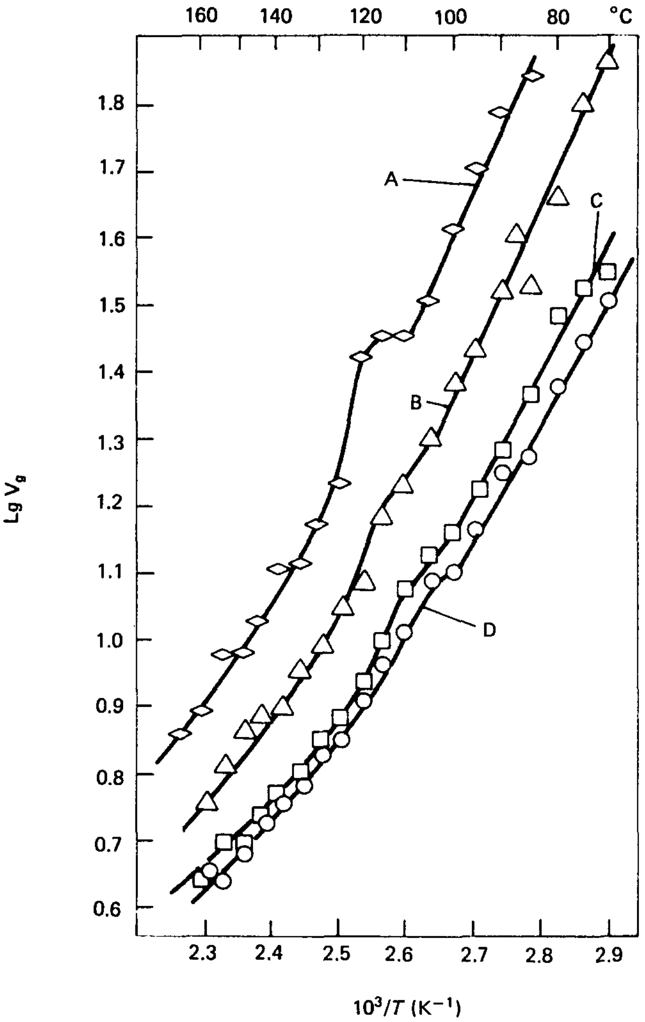

Figure 3 Retention diagrams for terpolymer PANB-II. A–D as in *Figure 2*

The ability of a sorbate to penetrate into copolymer depends on its molar volume and on its thermodynamic quality as a solvent of the polymeric material, i.e. it depends on the solubility of the sorbate in copolymer and on solvent–polymer interactions. The retention diagrams recorded for n-alcohols with AN/DVB copolymer are shown in *Figure 2*.

The change in the linear parts of the slopes in the retention volume vs. $1/T$ plot can be seen in both temperature ranges of segmental mobility characteristic for polyacrylonitrile. Small molecules of methanol or ethanol set in motion the rotations of segments in the paracrystalline regions whereas propanol and butanol did not. In the retention diagrams for the terpolymer containing 11 mol % BA (*Figure 3*) the points at which the slopes change for the two regions are both shifted towards lower temperatures.

Further information is presented in *Figures 4* and *5*. It can be seen that the points at which segmental motions set on in amorphous regions move towards low temperatures

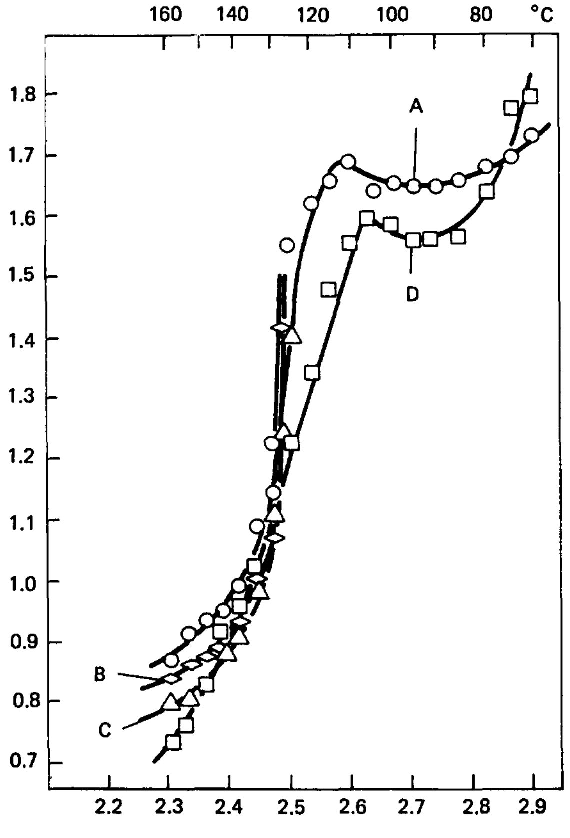

Figure 4 Retention diagrams for terpolymer PANB-III. A, methanol; B, butanol; C, propanol; D, ethanol

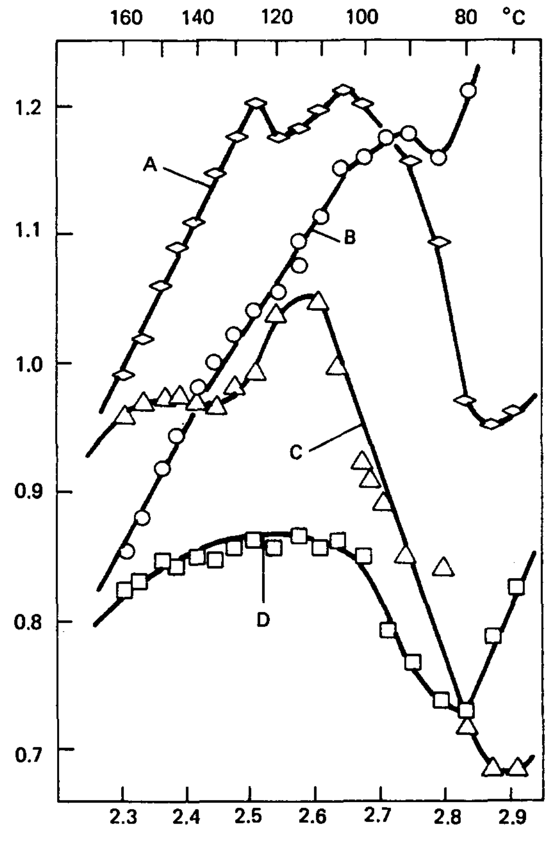

Figure 5 Retention diagrams for terpolymer PANB-IV. A, butanol; B, methanol; C, propanol; D, ethanol

roughly in proportion to the number of acrylate units in the terpolymers.

The true T_g which is probably due to the motions of segments in microgels remains unshifted at 122–125°C. This is consistent with T_g of styrene/DVB copolymers with 10% of DVB[25].

In the retention diagram for terpolymer PANE-VII which contains EA units, the respective deviations from linearity occur at higher temperatures than for terpolymers with BA (cf. *Figures 5* and *6*).

The temperature range at which T_g occurs also depends on the nature of the probe. A shift in such a range was

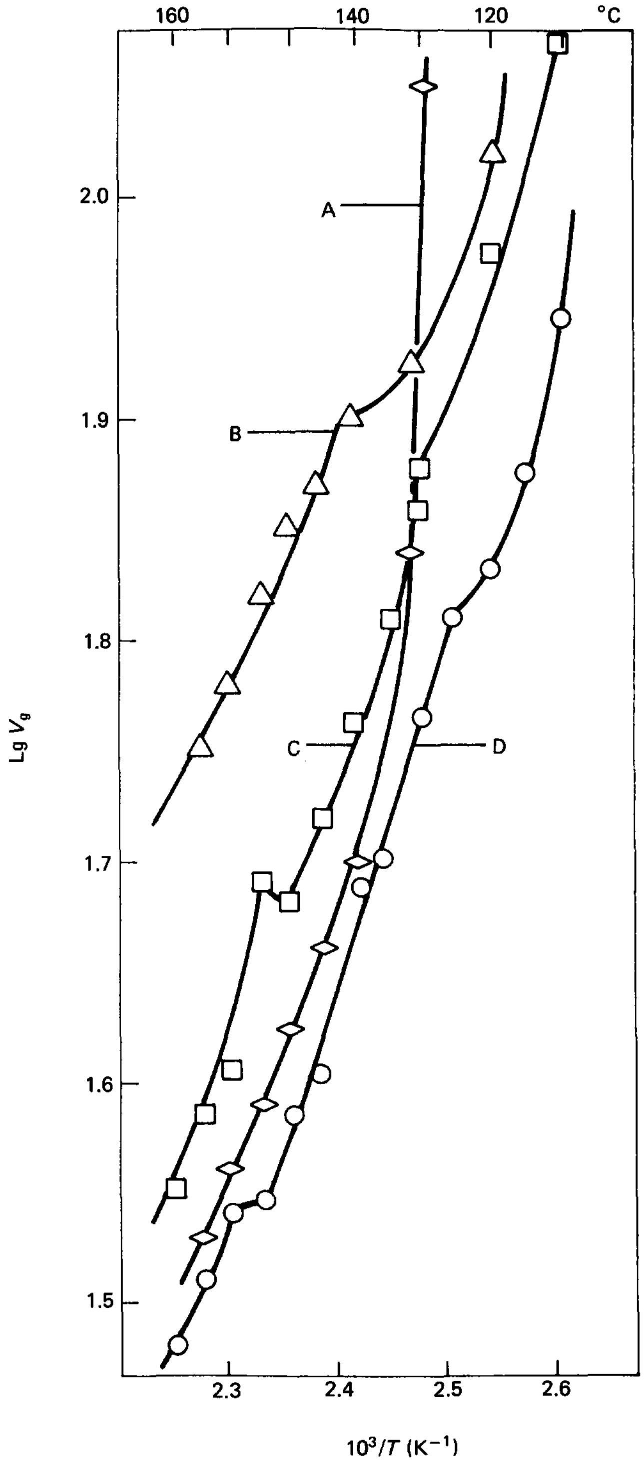

Figure 6 Retention diagrams for terpolymer PANE-VII. A, butanol: B, propanol; C, ethanol; D, methanol

observed for copolymers of styrene and DVB when various alcohols were used as probes[25].

As far as we know, no method has been developed for assessing the surface properties of porous copolymers in the swollen state. For these copolymers, the phase boundaries may disappear and the system becomes a one-phase system consisting of a single gel phase. The term 'expanded gel' is sometimes used to underline that the systems in swelling equilibrium may have regions with the same activity of the solvent as that of the solvent outside the system.

The polarity of the surface of crosslinked particulate copolymers is usually determined by gas chromatography by calculating the so-called Kovats indices[2,3]. This method, however, has its limitations. A linearity of the plot log retention time (t_R) vs. n, the number of carbon atoms in n-alkanes, is required. No such linearity was found for the present copolymers except for terpolymers PANB-II and PANB-III (*Table 5*).

For these two terpolymers, the dispersion component γ_s^D, of the surface energy was determined from the slope, s, of the relationship $\log t_R$ vs. n assuming that it is temperature independent and applying the following equation[26]:

$$s = \frac{2N}{RT} a_{CH_2} \gamma_s^{D\,1/2} \gamma_{CH_2}^{1/2}$$

where N is the Avogadro number, R is the gas constant, $T = 293$ K, a_{CH_2} is the surface area per CH_2 group (6×10^{-20} m^2) and γ_{CH_2} is the surface energy per CH_2 group (36 mJ m^{-2}).

The values of γ_s^D obtained by this method become smaller as the content of acrylate units in terpolymer PANB increases (*Table 5*). They are one order of magnitude smaller than those for AN/DVB copolymers. An increase of specific polymer–solvent interactions may be one of the reasons for this.

The terpolymer PANB is more hydrophilic than the AN/DVB copolymer. This can be deduced by comparing the water regain of the terpolymers (*Table 2*). The water regain is the sum of the mass of water filling macropores and of that in the gel phase. By assuming isotropic swelling[27], the fractions of copolymer in the gel (v_2) were calculated. These values become smaller as the number of acrylate units increases but v_2 for the gel-type BA/DVB copolymer is again very large (*Table 2*).

Table 5 Kovats indices and the dispersion components of surface energy, γ_s^D

			PANB	
Sorbate	Carbopak	40AN[a]	II	III
Benzene	561	770	1110	1160
Ethanol	296	645	975	1205
Methyl ethyl ketone	476	780	1150	1240
Nitromethane	378	830	1540	2020
Pyridine	547	985	1575	2000
γ_s^D (mJ m^{-2})	–	2.07	0.32	0.28

[a] See reference 2

CONCLUSIONS

The terpolymers AN, BA or EA and DVB containing 10 wt% of the crosslinking monomer preserve their porous structure in the condensed state until the content of acrylate units exceeds 50 mol%. Their porous structure, however, is not fixed and can be changed by an appropriate treatment before porosity measurements.

The terpolymers have a more hydrophilic structure than copolymers of AN and DVB.

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