Thermally Reversible Polymeric Sorbents for Acid Gases: CO_2, SO_2, and NOx

ABDERRAHMANE DIAF, JOSE L. GARCIA, and ERIC J. BECKMAN*

Chemical Engineering Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15261

SYNOPSIS

Weakly acidic gases such as CO_2, SO_2, NO_2, and NO discharged directly into the atmosphere have been suggested to contribute to the formation of acid rain and to global climate changes. In an effort to develop an effective process by which to remove these pollutants from gas streams, we synthesized polymeric sorbents that bind acid gases. In an earlier work, we reported that polymers carrying pendant amine groups are capable of absorbing carbon dioxide to form thermally reversible amine/CO_2 addition products. In this study, we investigated the effects of amine structure on acid gas sorption and the thermal reversibility of the sorption–desorption reactions of various acid gases including CO_2, SO_2, NO, and NO_2 with both linear and cross-linked polymers using thermogravimetric analysis. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

General public awareness concerning the protection of our environment has created the need to devise environmentally friendly and energy-efficient technology for the clean up of industrial gas streams. In addition, acidic gases such as CO_2 and SO_2 can act as poisons for various catalyst systems and thus must be removed from certain process streams. More than a century ago, Fileti and Puccini[1] reported that carbon dioxide reacts readily with strongly basic aryl-alkylamines to form products that they believed to be carbonates. From more recent investigations,[2-8] it is generally accepted that the reaction of CO_2 and amines can form either the zwiterion or ion/counterion products, depending upon the stoichiometry:

Formation of a zwiterion:

$$R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NH^+ COO^-$$

Protonation of amine:

$$R_1R_2NH^+ COO^- + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- R_1R_2NH_2^+$$

In the late 1950s and early 1960s, Drago and Paulik[9] reported that NO can behave as an electron-pair acceptor and thus can form NO/amine adducts whose thermal stability is a function of the basicity of the amine.[10] It is therefore conceivable that one could generate amino-functional polymers that would absorb not only CO_2 and NO, but also other Lewis acid gases such as NO_2 and SO_2.

Regeneratable polymeric sorbents for acidic gases can provide several advantages in industrial applications because they are environmentally benign, relatively stable, easy to handle (low density), and recyclable and can be regenerated under mild process conditions. In addition, the ability to prepare porous, cross-linked materials maximizes both the rate and ultimate capacity for sorption, significantly enhancing the potential of these materials for industrial applications. Our previous studies[11-13] showed that linear copolymers of styrene carrying pendant amino groups readily fix CO_2 at ambient conditions, reverting to the original amino polymer via a mild heat treatment. Recently, Tsuda et al.[14,15] reported on a wet process whereby amino-functional silica gels, suspended in *N,N*-dimethylformamide and in water, absorbed carbon dioxide effectively and reversibly. The dry-process polymeric sorbents prepared for this study were synthesized via chemical modification of a polymeric precursor using the following methods:

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 53, 857–875 (1994)
CCC 0021-8995/94/070857-19

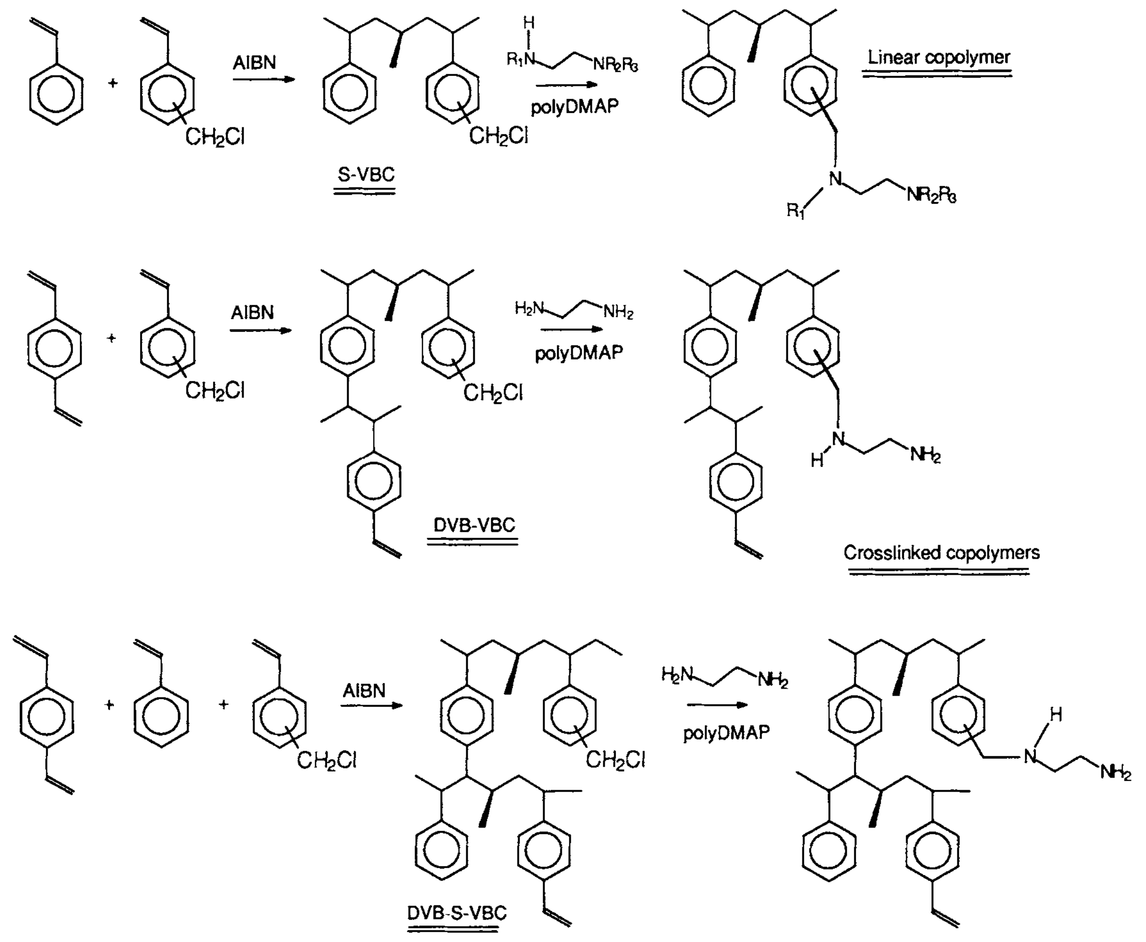


Figure 1 Scheme for synthesis of amino-functional, linear, and cross-linked polymers.

1. Amination of a series of styrene-*co*-vinylbenzylchloride (S–VBC) copolymers to produce linear amino-functional materials[16–18] with various amine contents and structures.
2. Solution polymerization of divinylbenzene–vinylbenzylchloride (DVB–VBC) and divinylbenzene–styrene–vinylbenzylchloride (DVB–S–VBC) systems resulting in a cross-linked polymer network (Fig. 1). Ethylenediamine (EDA) was then used to functionalize the precursors and thus produce EDA-functional, porous cross-linked beads.

EXPERIMENTAL

Synthesis of S–VBC Copolymers

Styrene and VBC (70% *meta*, 30% *para*) from Aldrich were washed separately with a 0.5% aqueous sodium hydroxide solution to remove the polymerization inhibitors, then rinsed with distilled water to eliminate all traces of the sodium hydroxide. Molecular sieves were added to the monomers, which were then stored at 4°C. Prior to polymerization, the monomers were distilled twice under vacuum (700 mmHg), at 40°C for styrene and 90°C for VBC.

The precursor copolymers were made in a toluene (Fisher) solution via free-radical polymerization initiated by azobisisobutyronitrile (AIBN, Aldrich). Typically, a 3000 mL, three-neck round-bottom flask mounted with a reflux condenser was flushed with nitrogen for 1 h. The reactor was then charged with 100 mL toluene; 76.6 g (736.5 mmol) styrene; 22.5 g (147.5 mmol) VBC, and a solution of 105 mg of AIBN in 10 mL of toluene. The mixture was stirred at room temperature for 30 min while bubbling nitrogen into the reactants. The nitrogen feed was then shut off and the reactor was immersed in an oil bath preheated to 105°C. After heating for 8 h, the copolymer was recovered by pouring the solution into a large volume (500 mL) of methanol (Fisher). The precipitate was separated by filtration, redissolved in chloroform (Fisher), and coagulated again in methanol. The product was washed with methanol and dried under vacuum at 80°C.

Copolymer composition was determined by elemental analysis at Galbraith Laboratories, Knoxville, Tennessee, and also via high-resolution proton-NMR (Brucker MSL300 instrument with a 5 mm high-resolution probe and deuterochloroform as a solvent). In the case of the proton-NMR analysis, copolymer composition was calculated from the relative intensities of the proton signal arising from the chloromethyl groups of the VBC repeat units. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) using a Waters 150-C instrument with tetrahydrofuran (Aldrich) as the carrier solvent. Weight-average molecular weights and polydispersities were found to range from 98,000 to 130,000 and 2.5 to 3.2, respectively. Glass transition temperatures (T_g) were evaluated with a TA 2000 thermal analysis system using a heating rate of 10°C/min. The T_g's of all the copolymers were determined from second scans.

Preparation of Amino Polymers

The alkylation reactions to produce aminated copolymers were carried out in a toluene solution at

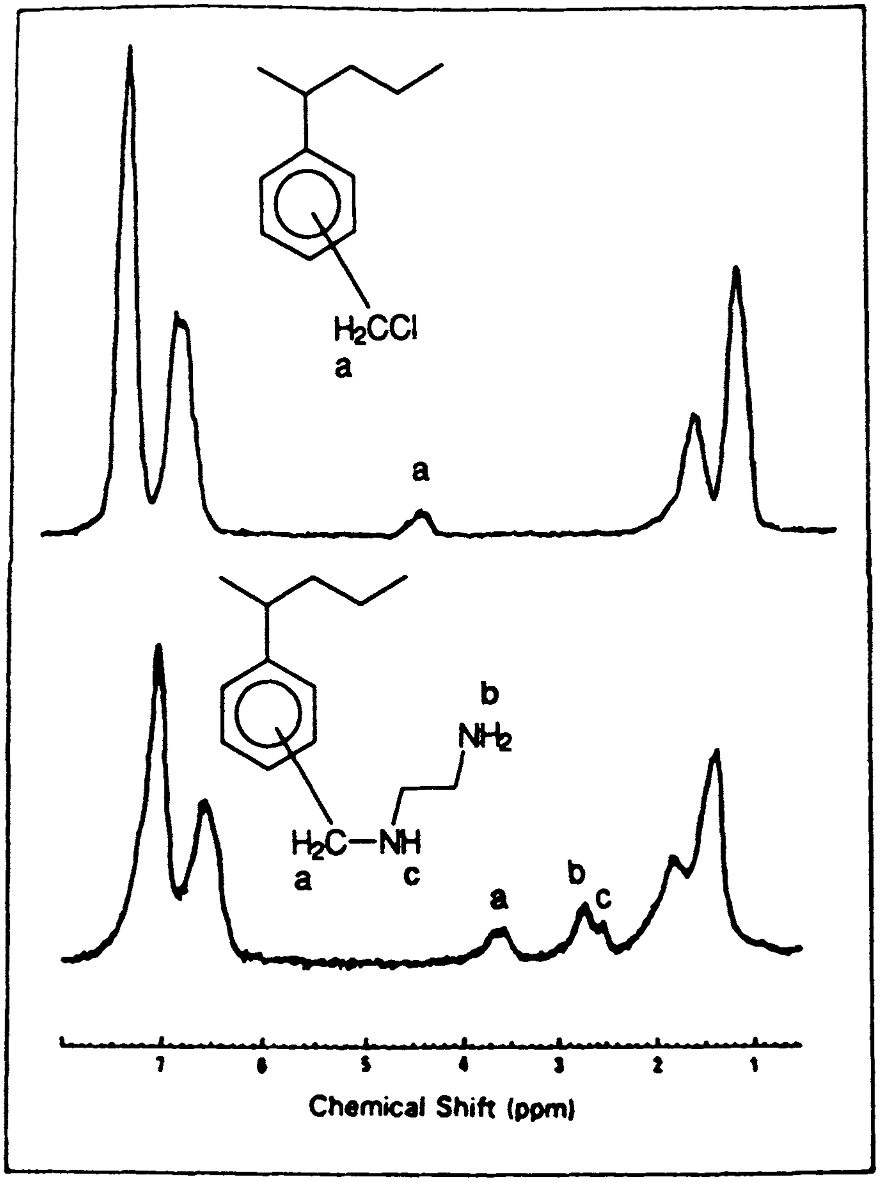
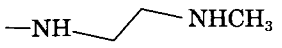
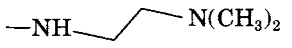
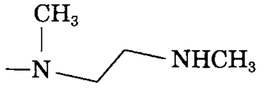
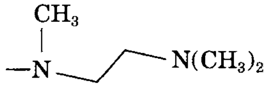
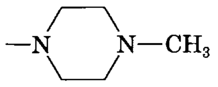


Figure 2 High-resolution ^{1}H-NMR of S–VBC and EDA-functional copolymers.

Table I Glass Transition Temperatures of Various Amino Polymers; Amino-functional Comonomer Mole Fraction: 0.23

Amine Type	Structure	T_g (°C)
EDA		92
N-Methyl EDA		90
N,*N*-Dimethyl EDA		91
N,*N'*-Dimethyl EDA		79
N,*N*,*N'*-Trimethyl EDA		90
1-Methylpiperazine		105
Dimethylamine	$-N(CH_3)_2$	118

30°C under nitrogen in the presence of a polymer-supported dialkylaminopyridine catalyst (PolyDMAP; Reillex Industries). In a typical experiment, 5.26 g of a S–VBC copolymer (with a 30% VBC molar content; thus, 13.3 mmol chlorine) were dissolved in 150 mL of toluene. Meanwhile, 8.92 g (149 mmol) of EDA (Aldrich) and 20 mL of toluene were placed in a 3000 mL, three-neck round-bottom flask previously flushed with nitrogen as indicated in the preceding section. The copolymer solution was added dropwise to the amine solution while stirring vigorously. The mixture was stirred for 48 h at 40°C, then heated to 80°C for 4 h. To recover the product, the reaction mixture was stirred vigorously with an equal volume of distilled water; then, the solvent was evaporated under vacuum and the water-insoluble fraction of the amino copolymer was separated by filtration, washed thoroughly with distilled water and methanol, then dried under vacuum. Preparation of materials functionalized with other EDA variants (e.g., *N*,*N'*-dimethylethylenediamine) was also accomplished following the same procedure.

Synthesis of DVB–VBC and DVB–S–VBC Cross-linked Beads

The polymerization inhibitors were removed from the monomers as described previously. DVB (Aldrich, 55% isomeric mixture; remainder is mainly 3 and 4-ethylvinylbenzene) was distilled twice at 40°C under vacuum (700 mmHg).

The cross-linked precursor was prepared in a toluene (Fisher) solution via a free-radical polymerization initiated by AIBN according to procedures described in the literature.[19] In a typical procedure, a 1000 mL three-neck round-bottom flask mounted with a reflux condenser was flushed with nitrogen for 2 h. The reactor was then charged with 54 mL toluene, 7 mL VBC (91.2 mmol), 4.33 mL DVB (49 mmol), 6.96 mL styrene (60.8 mmol), and a solution of 20 mg AIBN in 3 mL toluene. The reactor was immersed in an oil bath preheated to 105°C and stirred vigorously for 1 h. At the apparent onset of gelation, 50 mL toluene were injected into the reactor and the reaction was allowed to proceed for 3 additional h. The reaction mixture was poured into a large volume of methanol and the polymer was recovered by filtration, washed several times with methanol, redispersed in chloroform, and recoagulated in methanol. The product was then dried in a vacuum oven at 100°C.

Preparation of Amine-functional Cross-linked Beads

The cross-linked precursor beads were functionalized with EDA by nucleophilic substitution in a toluene solution (40°C) under nitrogen in the presence of a polymer-supported dialkylaminopyridine catalyst, (polyDMAP, Riellex Industries). Typically, 35 mL EDA (525 mmol, Aldrich) and 40 mL toluene were placed in a 250 mL three-neck round-bottom flask previously flushed with nitrogen. The suspension of DVB–VBC precursor (50 mL) was then added dropwise to the EDA solution while mixing. The slurry was stirred at 40°C for 48 h and then heated to 80°C for 4 h. To recover the product, the contents of the reactor were poured into a large volume of distilled water and stirred vigorously, after which the solvent was evaporated under vacuum. The polymer, in the form of a white light powder, was washed thoroughly with distilled water and methanol, then dried in a vacuum oven at 100°C.

The chemical composition of the cross-linked beads was determined by elemental analysis of nitrogen and chlorine at Galbraith Laboratories.[6] Fourier transform infrared spectroscopy (FTIR) (Mattson Polaris instrument) was also used to probe the chemical structure of the DVB/VBC precursor and the amino-functional product. Spectra were recorded using solid samples prepared in the form of KBr wafers. Bead porosity was assessed by electron microscopy and BET surface area.

Sorption of Acid Gases by Amino Polymers by Thermal Analysis

Reactions of acid gases (CO_2, SO_2, NO_2, and NO) with polymer-anchored amines were followed using the Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments) by directly exposing the polymer powder to pure CO_2 and a series of several mixtures (with nitrogen) as purge gases. Because the amino polymers fix CO_2 when exposed to the ambient air, polymers were thermally regenerated prior to all sorption studies. The linear copolymers were regenerated at a temperature 5°C below their T_g's in the TGA under dry nitrogen, while the cross-linked beads were heat-treated at 105°C. Equilibrium sorption of acid gas was considered to be attained when no weight change within the sensitivity limits of the instrument was detected within a 60 min time interval.

RESULTS AND DISCUSSION

Styrene-co-vinylbenzylchloride Copolymers

The reactivity ratios reported in the literature[20,21] for a S–VBC system suggest that this copolymerization should proceed randomly. Differential scanning calorimetry (DSC) measurements using the TA 2910 system revealed a single glass transition temperature that varied predictably with copolymer composition, typical behavior for a random copolymer within the sensitivity limits of the DSC technique to fine structure.[12]

Linear Amino-functional Copolymers

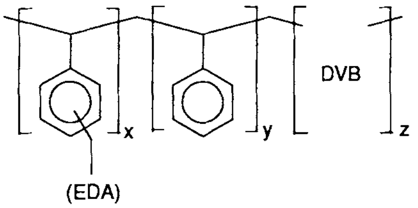
The nitrogen and residual chlorine (trace amounts) contents of the aminated copolymers as evaluated by Galbraith Laboratories are in agreement with the NMR spectra (Fig. 2), which suggest quantitative conversion to amino-functional copolymers. The glass transition temperatures of the amino-functional copolymers were found to be a function of amine structure, as shown in Table I, and amine content as indicated in Figure 3. As can be seen in Figure 3, low amounts of the EDA-functional comonomer act to plasticize the polymer, lowering the T_g from 101°C (polystyrene) to 80°C at 40 mol %, whereas further addition of the EDA-functional comonomer dramatically increases the T_g, such that a 50/50 copolymer exhibits a T_g of 103°C, and copolymers with higher functional comonomer content

Table II Chemical Composition of the Cross-linked Sorbents

	Bead 1	Bead 2	Bead 3	Bead 4
DVB (mL in feed)	7	7.5	7	7
VBC (mL in feed)	13	10	3	8.7
Styrene (mL in feed)	0	0	0	3.5
Nitrogen content (wt %)[a]	7.8	5.9	3.6	3.7
Chlorine content (wt %)[a]	0.7	1.2	0.8	0.1
x^b	0.42	0.31	0.18	—
y^b	0.03	0.05	0.03	—
z^b	0.55	0.64	0.79	—
Conversion (mol %)[c]	93	86	86	98

[a] Evaluated by elemental analysis.

[b] See structure below:



[c] Based on the molar conversion of chloromethyl to amine-functional groups.

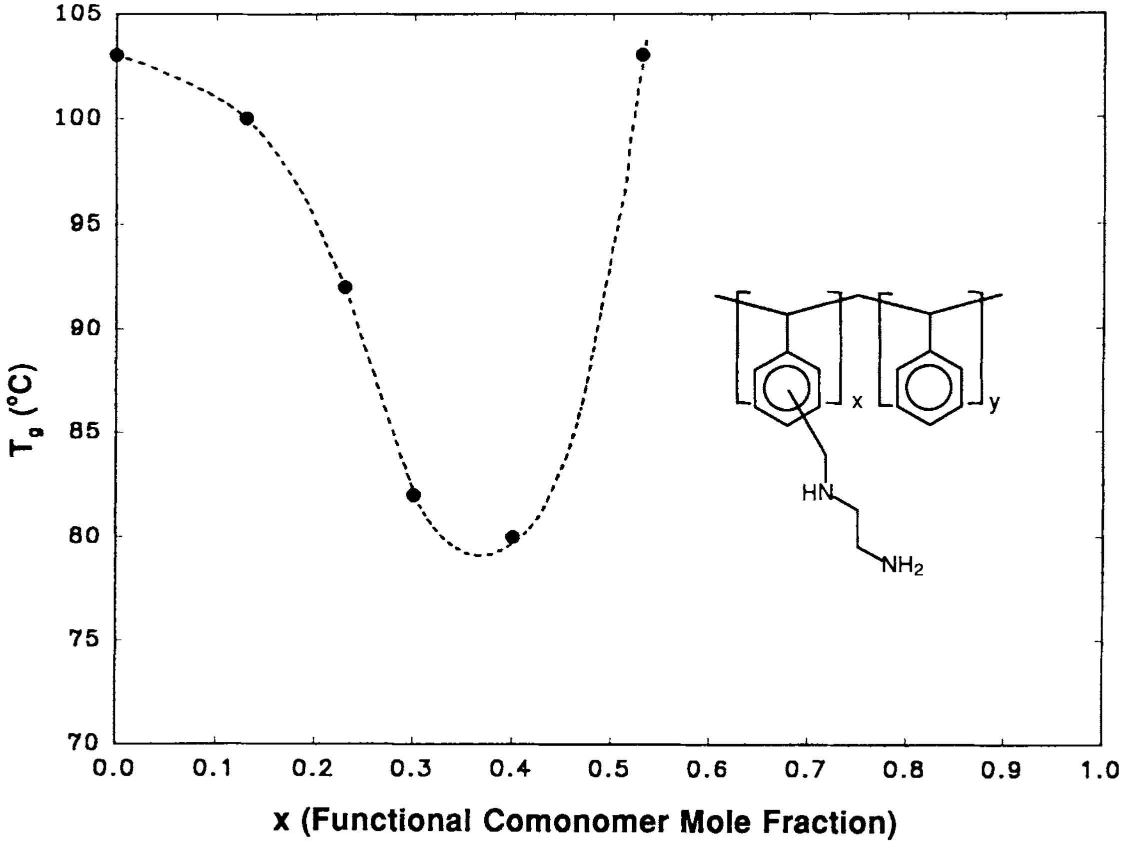


Figure 3 Glass transition temperature of EDA-functional copolymers.

(60, 75, and 100%) did not show any glass/rubber transition within the range of −60 to 300°C. Cross-linking is not likely to be the origin of this T_g behavior since these copolymers were soluble in toluene and no cross-linking reaction is observed during DSC scans. At this point, we can only speculate that this unusual behavior may be rationalized by a loss in chain mobility caused by strong electronic donor–acceptor interactions between the phenyl and amine groups. TGA measurements revealed that these materials undergo no weight loss up to 300°C under nitrogen, indicating a thermal stability comparable to that of a styrene homopolymer.

Cross-linked Amino-functional Beads

The chemical compositions of the polymer precursors and the amino-functional cross-linked beads were determined via elemental analysis of nitrogen and chlorine. The results of these measurements (Table II) indicate that as the mole fraction of the cross-linker (DVB) increases the conversion of chloromethyl to an amino-functional product decreases, probably because the higher cross-link density limits the degree of swelling of the beads by the amine solution. Consequently, styrene was added to the network as VBC content decreased to maintain similar cross-link densities and thus to ensure similar chemical structures. Conversion of chloromethyls to amino groups thus increased to near quantitative values (Table II).

Typical FTIR spectra (Fig. 4) of solid KBr/copolymer wafers indicate the formation of an amine-functional product, as evidenced by the medium intensity doublet band centered at 3350 and 3300 cm^{-1} (primary N—H stretch) and the characteristic C—N stretch band at 1120–1110 cm^{-1}. Further, spectra of the DVB/VBC and the DVB/S/VBC cross-linked precursors revealed a weak medium intensity absorption band at 1630–1620 cm^{-1} (C═C stretch), which indicates the presence of residual double bonds of DVB units incorporated into the polymer. These results are in agreement with the well-known fact that the first vinyl group of DVB is highly reactive (more reactive than styrene, $r_1 = 1.18$ and $r_2 = 0.26$ for a DVB–S system,[22]) whereas the second double bond is much less reactive. In fact, literature results[23] showed that up to 50% of

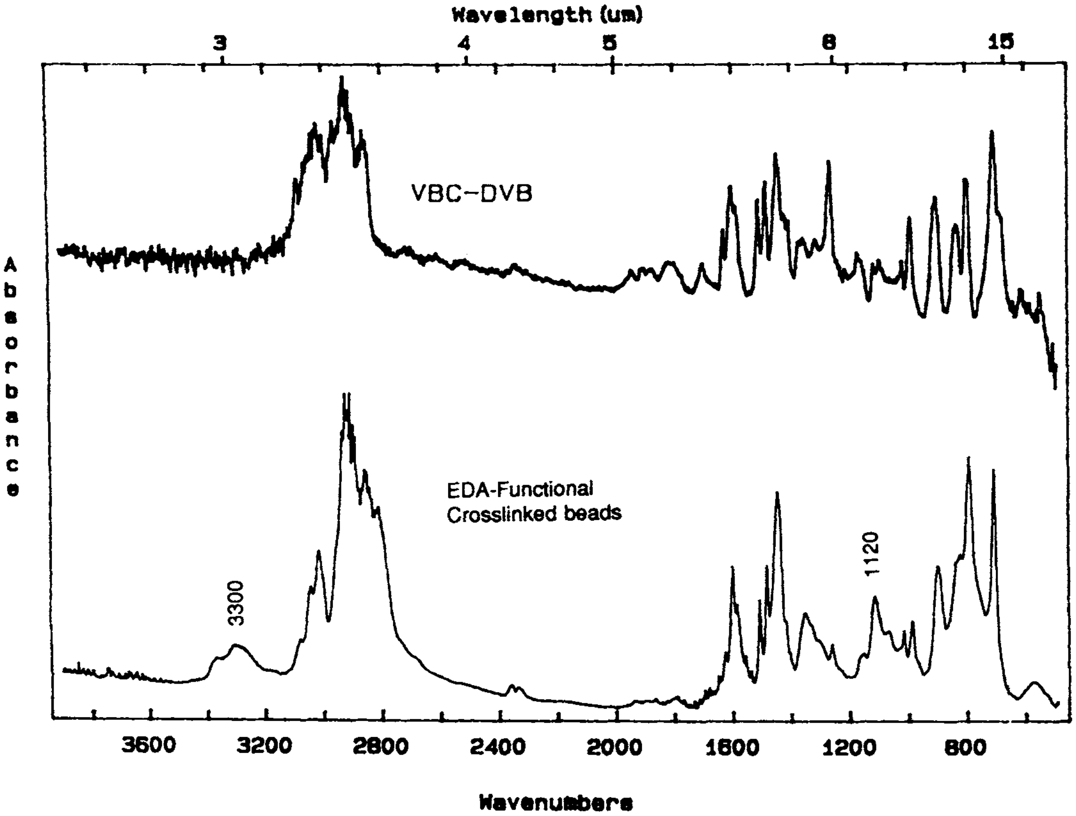


Figure 4 FTIR spectra of VBC–DVB and EDA-functional cross-linked beads.

the DVB second double bonds can remain intact in the cross-linked product. In the case of a DVB/VBC or a DVB/S/VBC system, although there are no kinetic data to our knowledge on the reactivity ratios for these systems, it is, however, clear from the FTIR spectra that a fraction of the DVB incorporated into the product does not participate in the building of the cross-linked network but takes on the role of a spacer entity, as is also the case for the isomeric units of ethylvinylbenzene. In view of the elemental analysis results (Table II), the DVB/(VBC + VB amine) molar ratio in the cross-linked polymer is higher than the DVB/VBC monomer mole ration in the feed, leading to the conclusion that DVB is also more reactive than is VBC. Thermal analysis of cross-linked DVB/VBC and DVB/S/VBC beads revealed no state transition within −80 to 300°C and no weight loss up to 300°C.

Scanning electron micrographs (Fig. 5) of the cross-linked amino-functional beads revealed a highly porous texture of their polymer matrix. BET surface areas measured by the liquid nitrogen sorption technique gave values in the range of 50 m^2/g, whereas their linear counterparts averaged a value of 30 m^2/g.

Cyclic Sorption–Desorption of Acid Gases

Carbon Dioxide

Both linear polymers and cross-linked beads were exposed to CO_2 and a 14% CO_2/N_2 mixture (a typical CO_2 concentration in combustor stack emissions) in the TGA at various temperatures ranging from 25 to 105°C. In general, amino-functional polymers show a high affinity for CO_2 and, thus, readily form addition products upon exposure to the gas, even to the point of absorbing CO_2 from ambient air (i.e., at a concentration in the 200 ppm range).

FTIR spectra (Fig. 6) of amino polymers exposed to CO_2 showed absorption bands of carboxylate residues (at 1650 and 1420 cm^{-1}), whereas the TGA results of the linear polymers functionalized with various EDA variants (structures shown in Table I) suggest that, on average, each primary amine binds 0.18 CO_2 molecules, secondary amine 0.07 CO_2's, and tertiary amine 0.02 CO_2's. These results indicate that primary amines are stronger nucleophiles than are secondary and tertiary amines toward Lewis acids. Thus, in general, Lewis basicity of amino-functional polymers increases in the following order: primary > secondary > tertiary. Re-

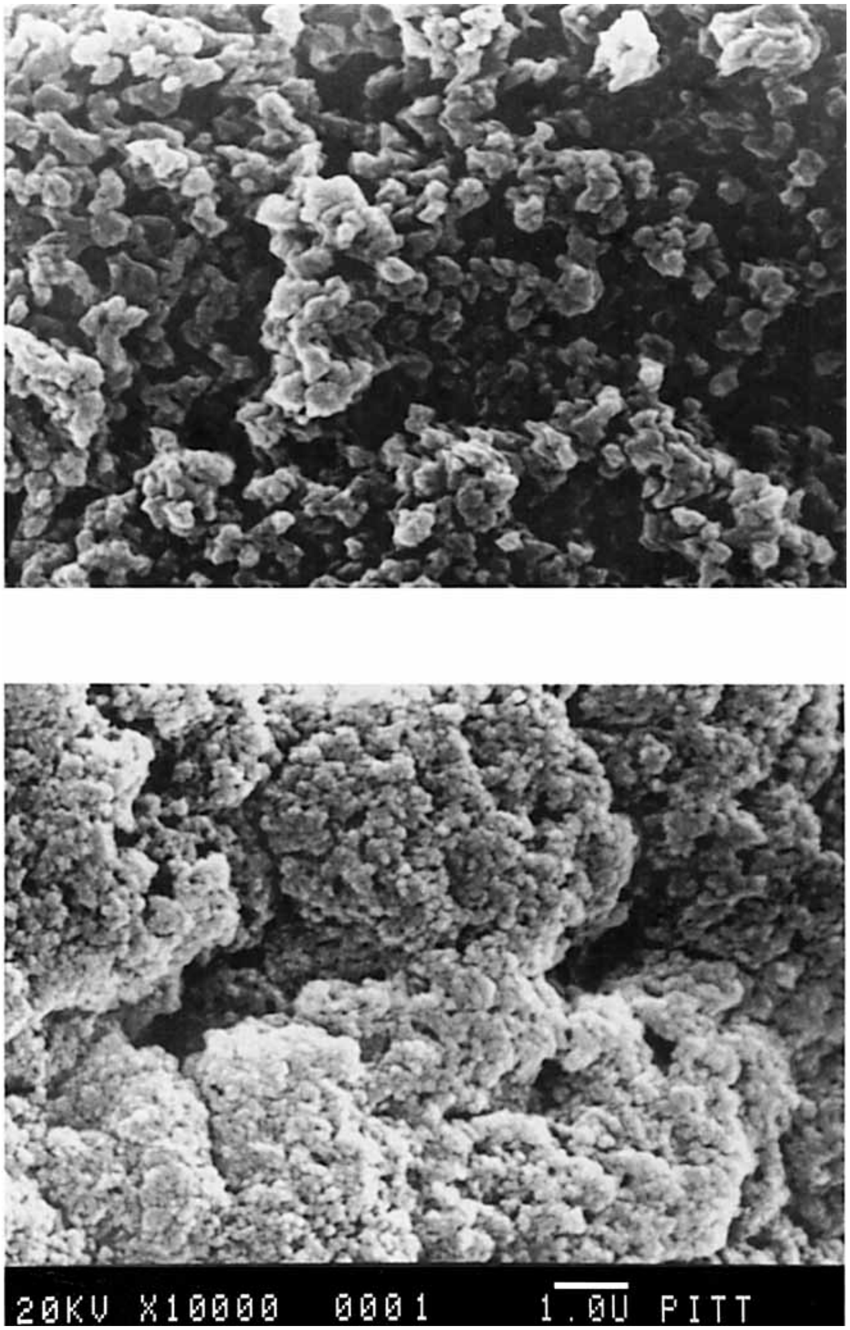


Figure 5 SEM micrograph of EDA-functional cross-linked beads.

markably, polymer-anchored tertiary amines were found to absorb CO_2, albeit a small amount, whereas low molecular weight tertiary amines do not form addition products with the gas.[24] Reference runs using a styrene homopolymer and also a S–VBC precursor showed no weight increase upon exposure to CO_2.

Cyclic exposure of the beads to pure CO_2 and several CO_2–nitrogen mixtures in the TGA showed that the sorption–desorption reactions are thermally reversible, as also evidenced by the FTIR spectra (Fig. 6) of the virgin material and the exposed samples before and after regeneration. Further, we would expect that deactivation of amine sites owing to thermal cycling would involve formation of urea bridges/cross-links, with the concomitant loss of water during the reaction. FTIR spectra recorded after CO_2 exposure/thermal cycling showed no signs of urea

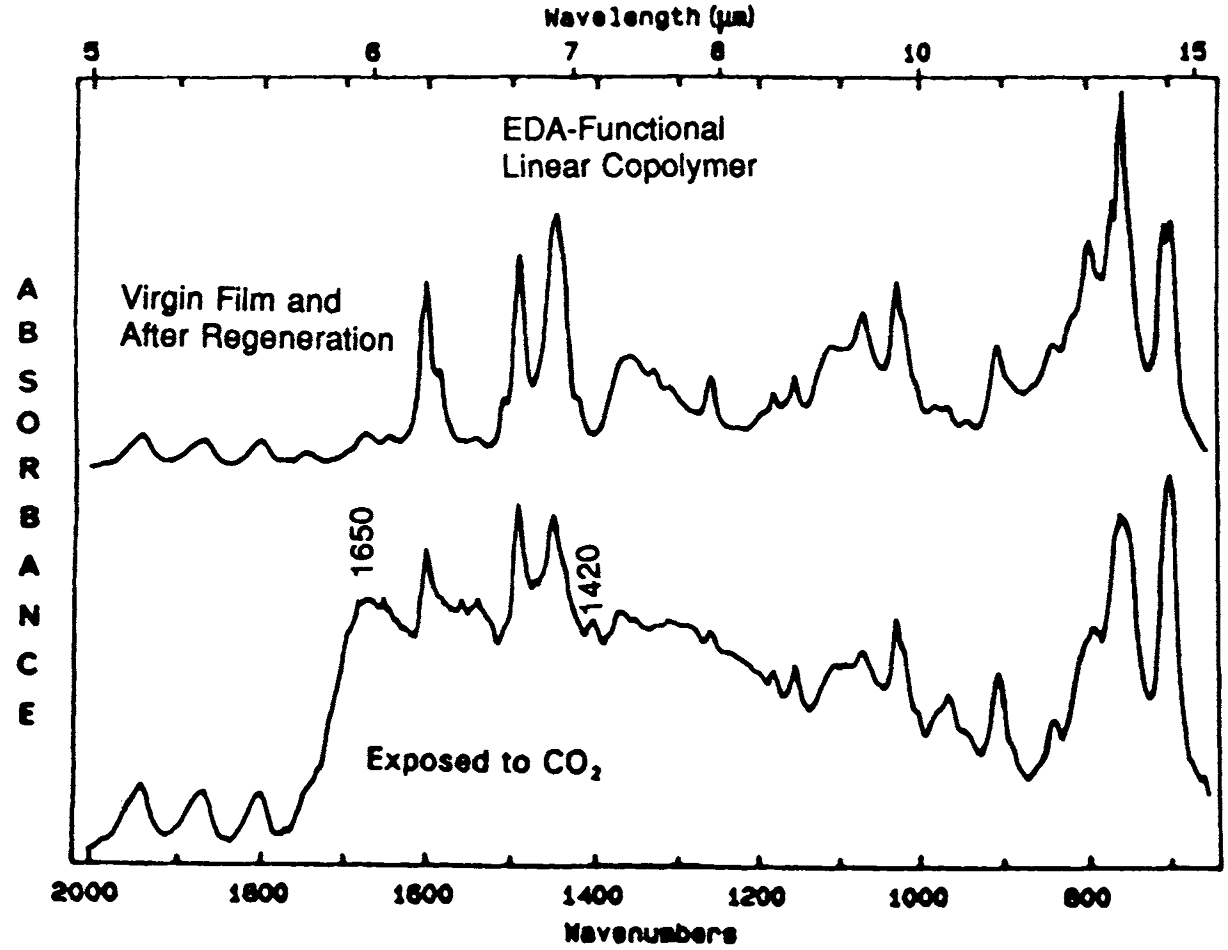


Figure 6 FTIR spectra of EDA-functional linear copolymer; upper curve is film following several CO_2-sorption/desorption cycles (identical to spectrum of virgin copolymer); lower curve is film after CO_2 exposure alone.

formation. In addition, analysis of the composition of the off-gas during thermal regeneration of the amino polymers (after CO_2 exposure) using the Dycor mass spectrometer showed no evidence of water production (as would be expected in the event of urea formation) during CO_2 exposure/thermal cycling. Finally, we found that the sorption capacity of the amino polymers does not change from one cycle to the next (Fig. 7).

The effects of the functional comonomer mole fraction and porosity on the ultimate CO_2 sorption capacity was determined under the same contacting conditions between the gas and the EDA-functional copolymers (both linear and cross-linked). As would be expected, the porous cross-linked beads showed a higher CO_2-sorption capacity (Fig. 8) than that of the linear copolymers owing to a higher concentration of accessible amine sites. Further, as the amine content increases, the CO_2-sorption capacity increases, then starts leveling off at 45–50 mol % of the functional comonomer for the linear copolymers. The sigmoidal shape of the curve can be rationalized by the fact that the CO_2 diffusion coefficient (evaluated from the TGA data using a model developed by Souchay and Pannetier[25]) goes through a maximum (Fig. 9) at 40–50 mol % of the functional comonomer, revealing the onset of CO_2 barrier properties of the adducts.

Given that the reaction between CO_2 and amines is exothermic, we would expect that the equilibrium sorption capacity of the polymers will decrease with increasing temperature, as is indeed the case (Fig. 10).

Sulfur Dioxide

Amino polymers, both linear and cross-linked, were exposed to a 1% SO_2/N_2 mixture in the TGA at

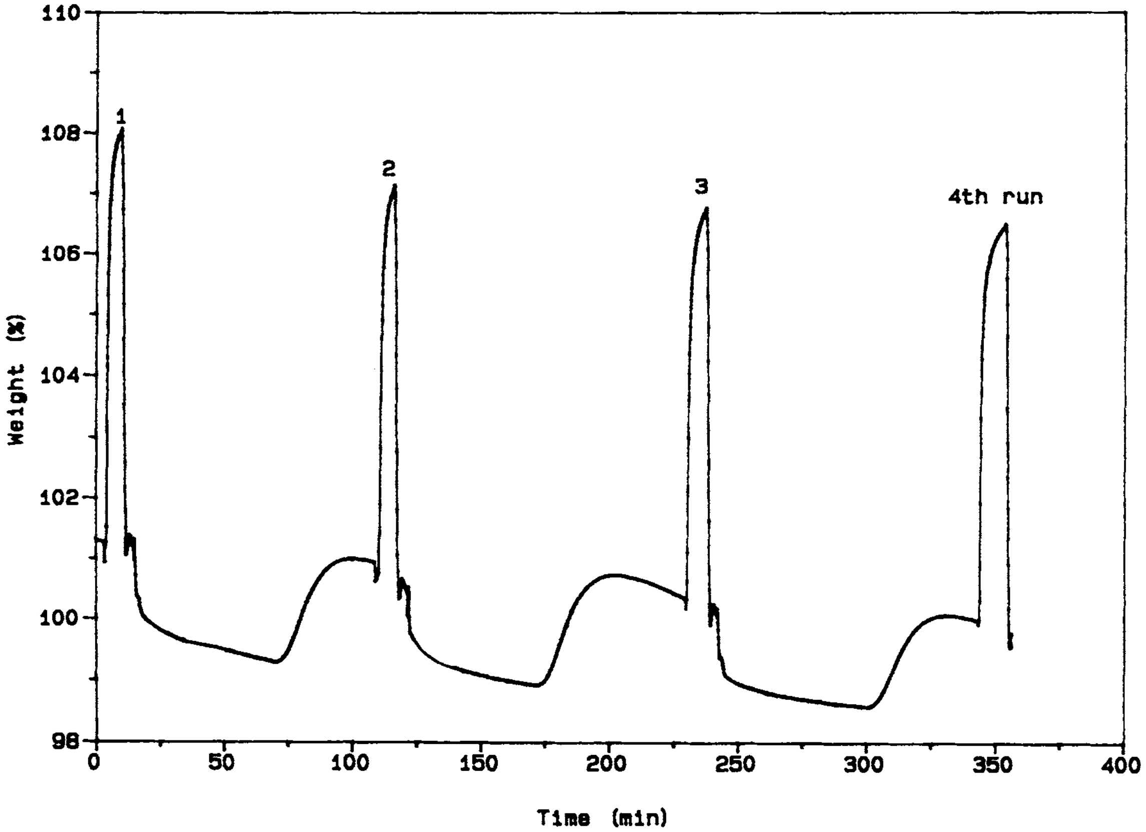


Figure 7 Cyclic CO_2 sorption/desorption using EDA-functional cross-linked beads.

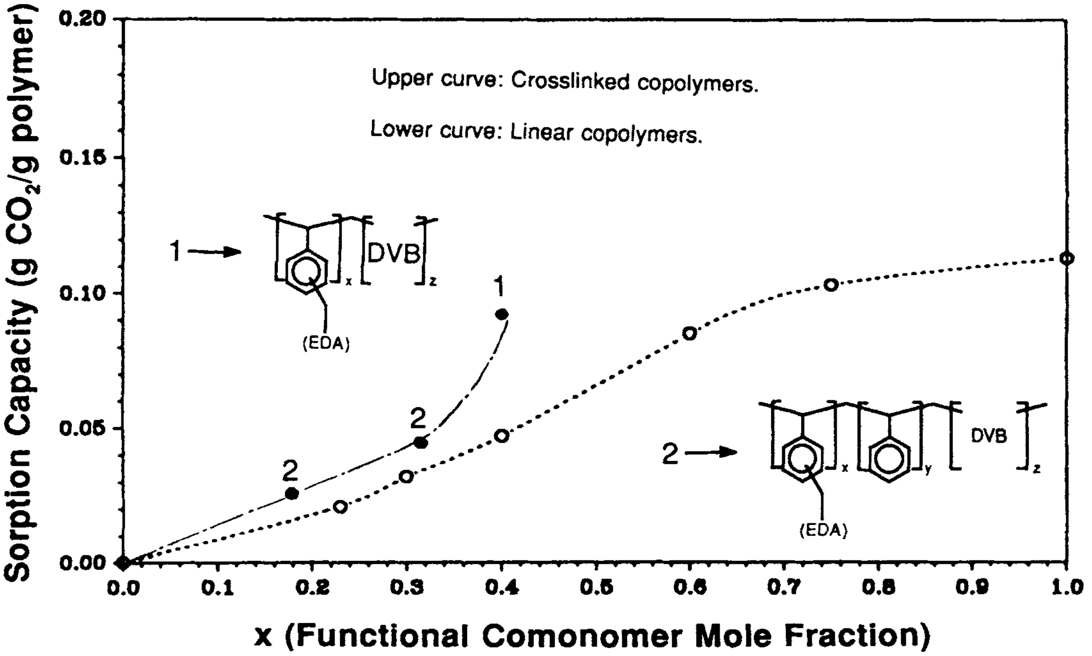


Figure 8 CO_2-sorption capacity of EDA-functional copolymers vs. amine content.

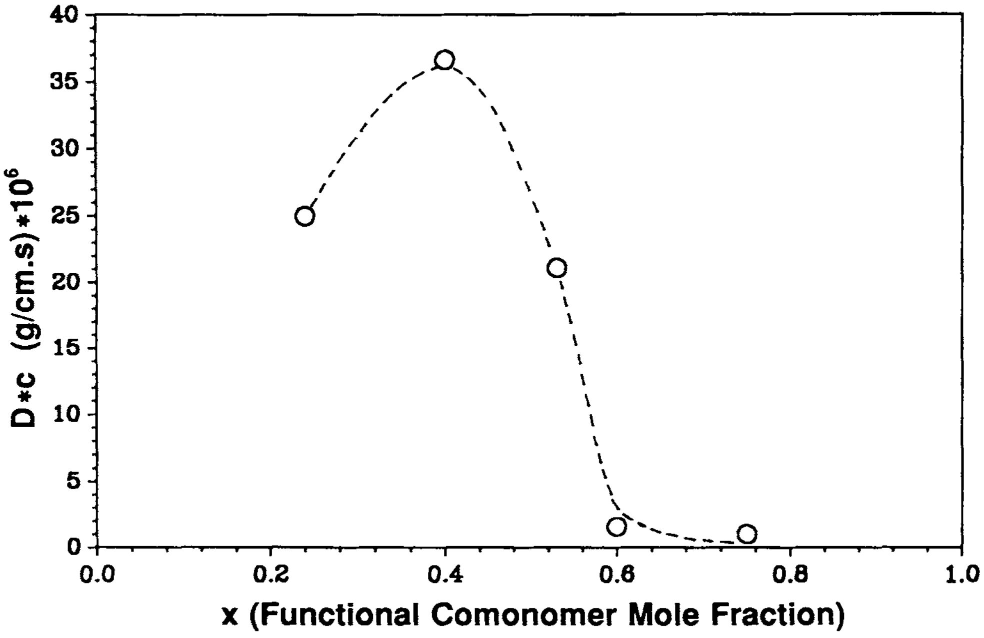


Figure 9 Effect of amine content on CO_2 diffusion through the polymer matrix.

25°C. The results of this study showed that both the linear and the cross-linked beads have a high affinity for SO_2. FTIR spectra (Fig. 11) of the virgin polymers and the exposed sorbents before and after regeneration suggest that the SO_2 sorption mechanism by which the SO_2 adduct is formed is similar to that of CO_2, i.e.:

$$R_1R_2NH + SO_2 \rightleftharpoons R_1R_2NH^+ \, SO_2^-$$

where R_1 and R_2 = H or CH_3. In support of the proposed scheme is the fact that polymers carrying tertiary amines such as *N,N,N'*-trimethylethylenediamine (*N,N,N'*-TMEDA) and 1-methylpiperazine (1-MPip) (no transferable proton) were also found

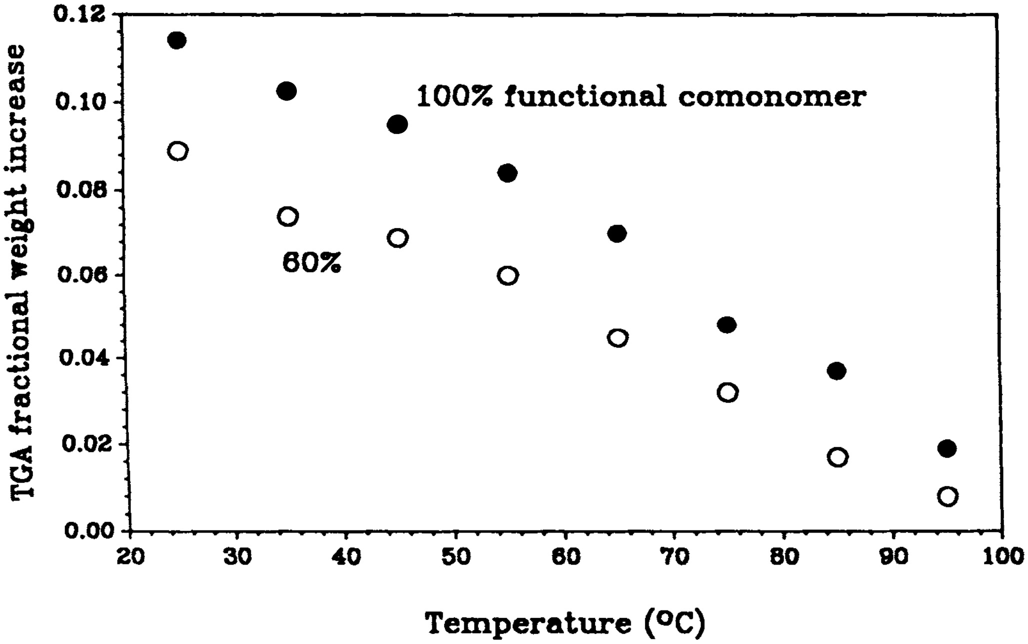


Figure 10 CO_2-sorption capacity of linear copolymers vs. temperature.

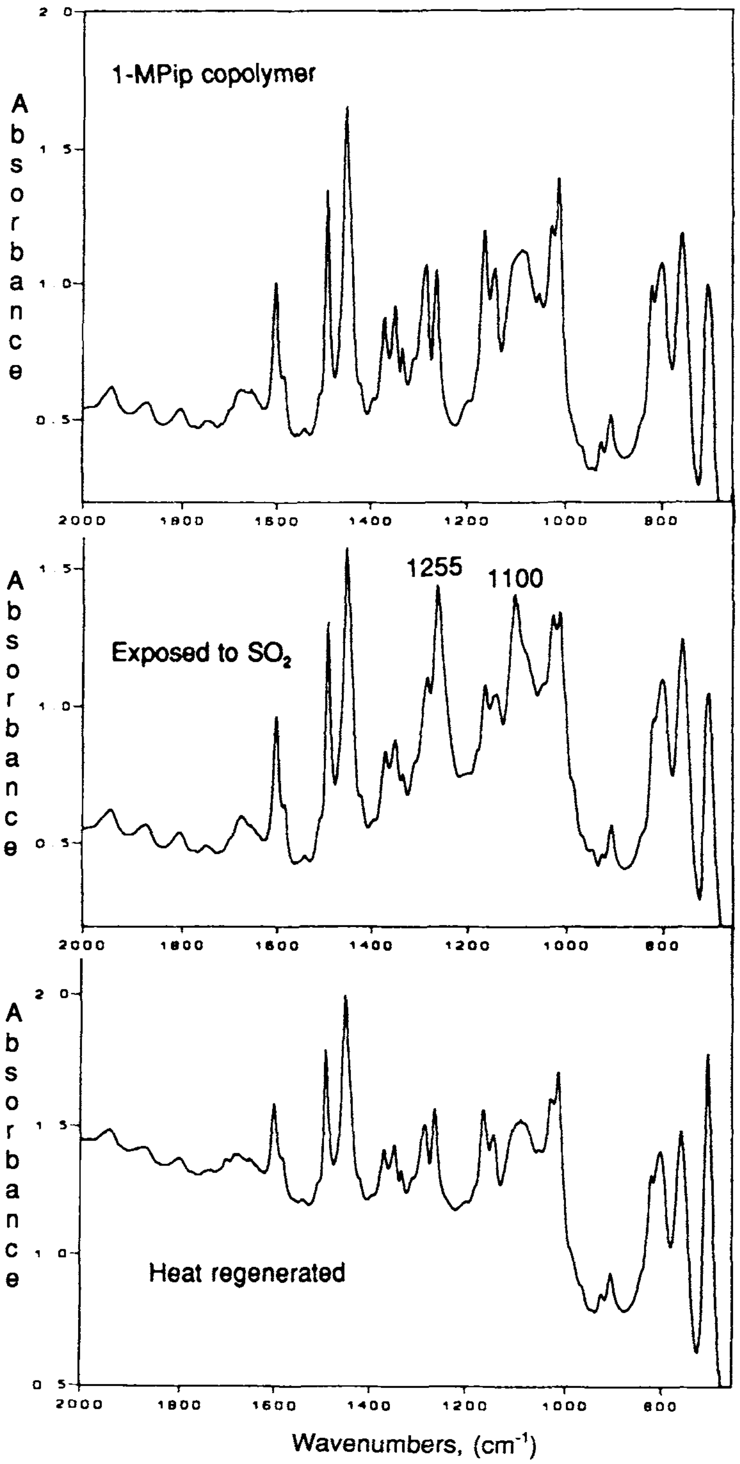


Figure 11 FTIR spectra of linear copolymer functionalized with 1-methylpiperazine (upper curve), exposed to SO_2 (middle), and after heat-regeneration (lower curve).

to absorb SO_2 (Fig. 12). On average, the TGA results showed that the linear copolymers functionalized with EDA, 1-MPip, and *N,N,N'*-TMEDA (23% molar of functional comonomer) bind 0.25, 0.21, and 0.20 SO_2 molecules per nitrogen atom, respectively. Surprisingly, unlike the CO_2 sorption process, the SO_2 ultimate sorption capacity increases linearly with amine content (Fig. 13). Further, amino poly-

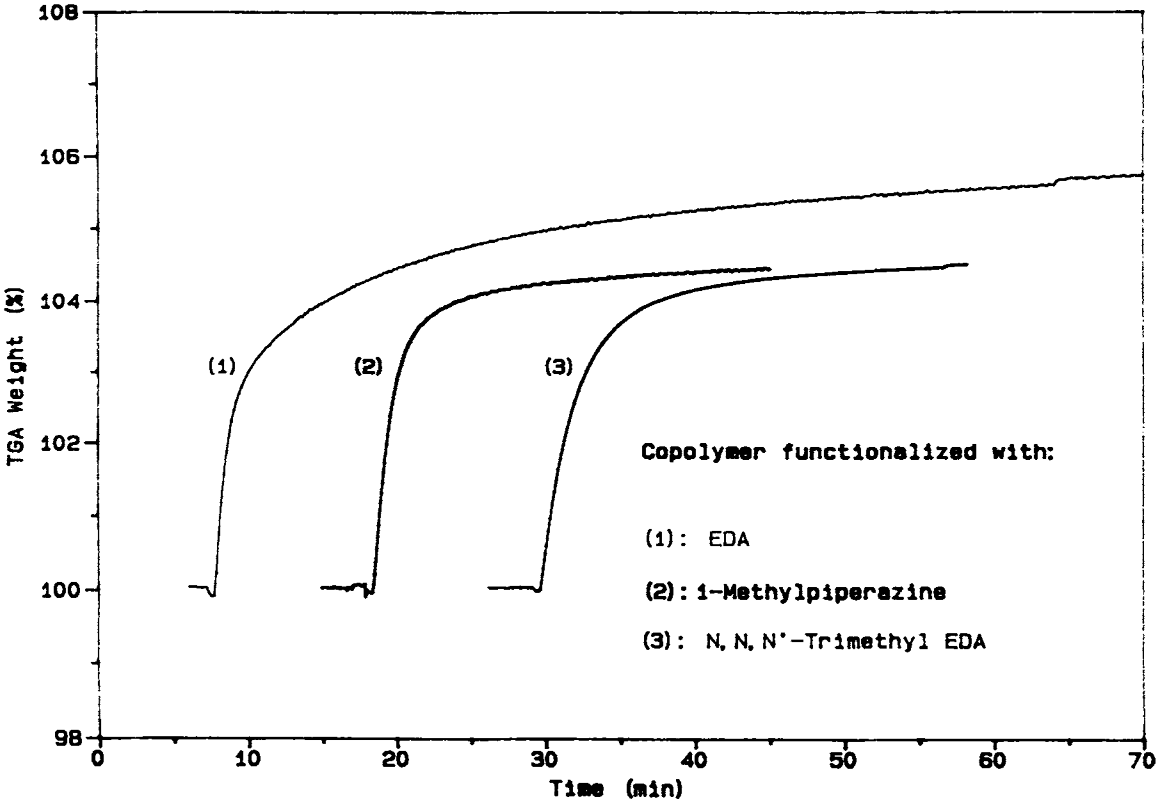


Figure 12 SO_2-sorption isotherms of amino-functional copolymers.

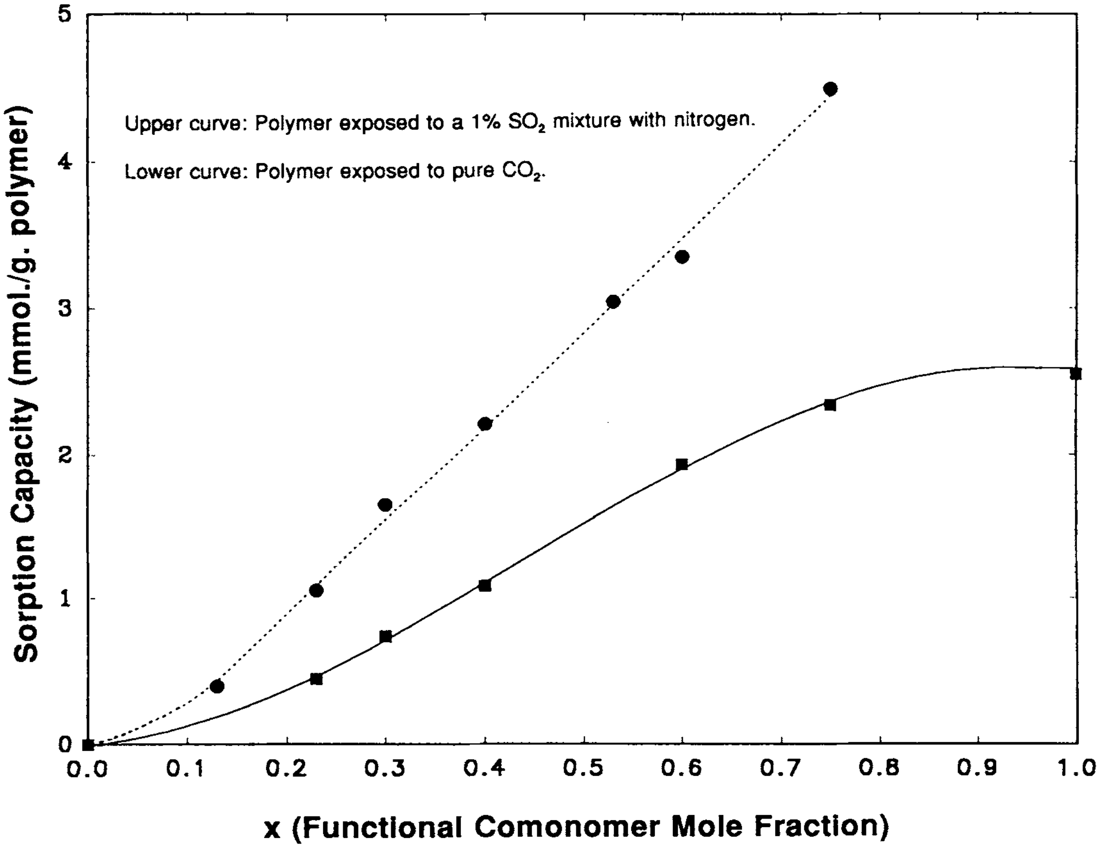


Figure 13 SO_2-sorption capacity of EDA-functional copolymers vs. amine content.

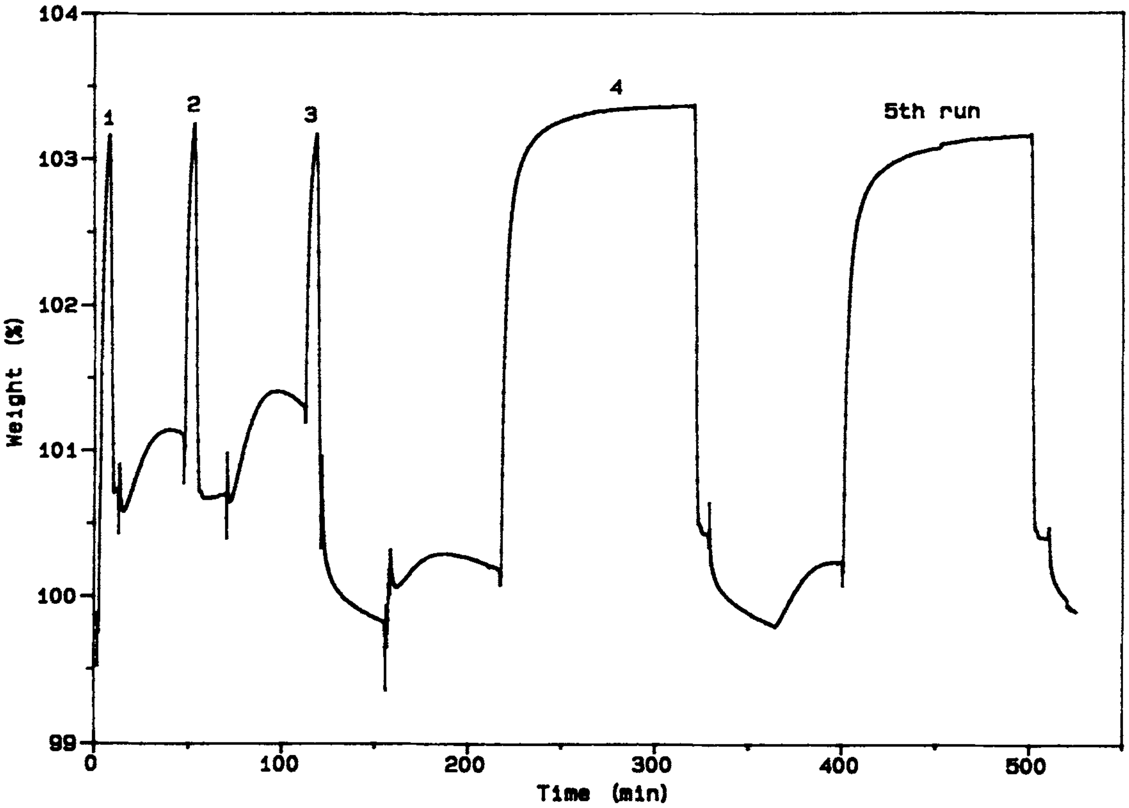


Figure 14 Cyclic SO_2 sorption/desorption using a tertiary amine-functional copolymer.

mers exhibit a much higher affinity for SO_2 than for CO_2 (Fig. 13), owing, presumably, to the stronger Lewis acidity of SO_2. The SO_2 addition products formed with the primary, secondary, and tertiary amino-functional polymers were found to dissociate slowly under nitrogen at ambient conditions. The dissociation of the adducts may be accelerated by a mild heat treatment. Cyclic exposures to SO_2 in the TGA showed that the sorption–desorption reactions are thermally reversible (Fig. 14). Here, also, no weight increase was detected when polystyrene and S-VBC polymers were exposed to SO_2.

Nitrogen Oxides

Amino polymers were exposed to N_2O as a 2% mixture in nitrogen, to NO as a 0.5% mixture, and to NO_2 as a 0.5% mixture. The TGA experiments showed that nitrous oxide does not form any addition products with amino-functional polymers. On the other hand, both the linear and the cross-linked polymeric sorbents were found to absorb nitric oxide, presumably via a mechanism first proposed by Drago and Paulik[9]

$$R_1R_2NH + NO \leftrightarrows R_1R_2NHNO \quad \text{slow}$$

$$R_1R_2NHNO + NO \leftrightarrows R_1R_2NHN_2O_2 \quad \text{fast}$$

$$R_1R_2NHN_2O_2 + R_1R_2NH \rightarrow R_1R_2NH_2^+ \, R_1R_2NN_2O_2^- \quad \text{fast}$$

In the absence of oxygen, previous studies have shown that NO reacts with low molecular weight primary and secondary amines under specific reaction conditions of temperature and pressure to form adducts whose thermal stability is a function of the basicity of the amine.[10] However, in the presence of oxygen, the amine/NO adducts oxidize to ammonium nitrites and nitrosamines[26]:

$$R_1R_2NH_2^+ \, R_1R_2NN_2O_2^- + \tfrac{1}{2}O_2 \rightarrow R_1R_2NH_2^+ \, NO_2^- + R_1R_2NNO$$

The study of nitric oxide sorption using the linear and the cross-linked sorbents showed that addition products are formed in both instances although the reaction proceeds at a relatively very slow rate (1.4% weight increase after 100 min of exposure to the

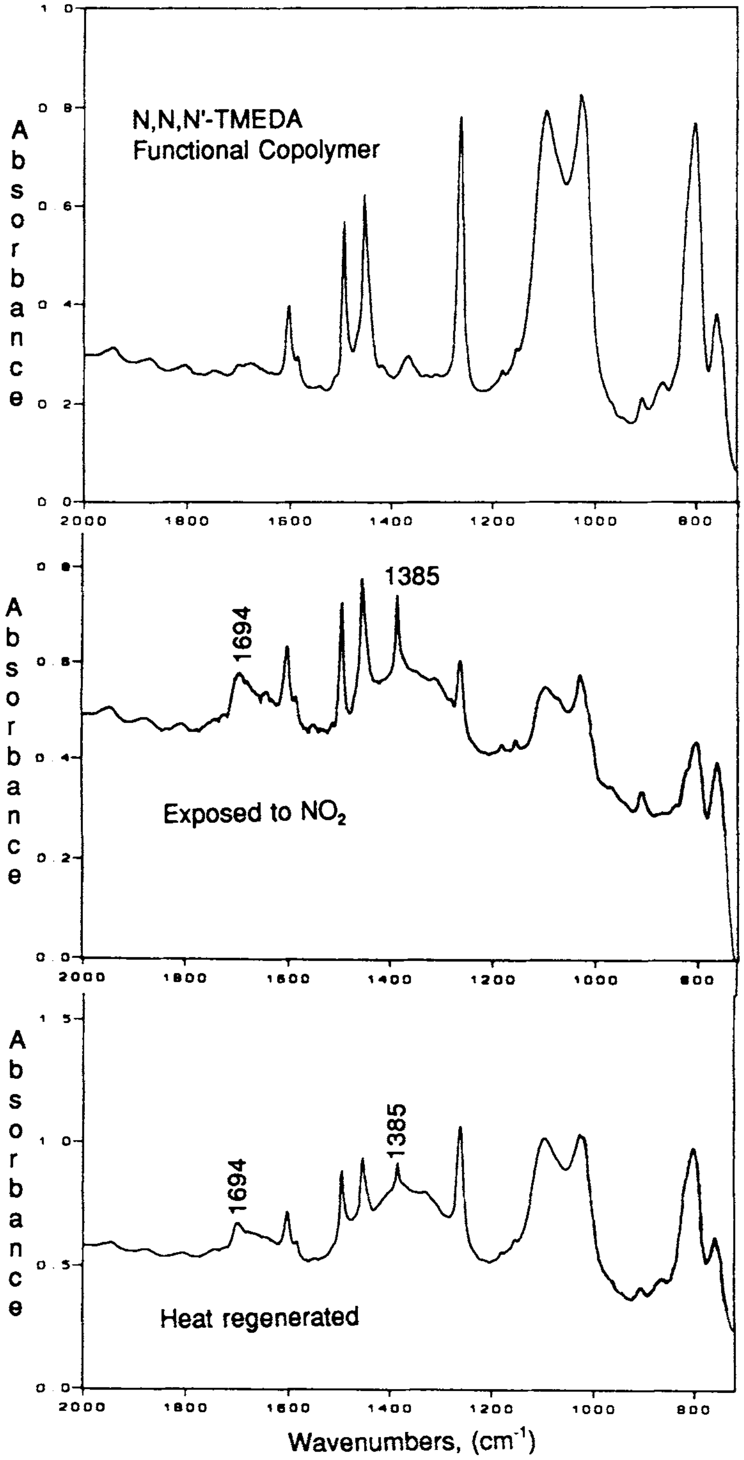


Figure 15 FTIR spectrum of EDA-functional copolymer exposed to NO_2.

NO/N_2 mixture) at ambient conditions, presumably owing to thermodynamic limitations, in that low temperatures are more favorable for high yields of NO/amine adducts.[27] The TGA results showed that, on the average, the EDA, *N,N,N'*-TMEDA and 1-MPip copolymers absorb 0.12, 0.02, and 0.20 NO molecules per nitrogen, for sorbents with 23 mol % of the functional comonomer. Further, the sorbents

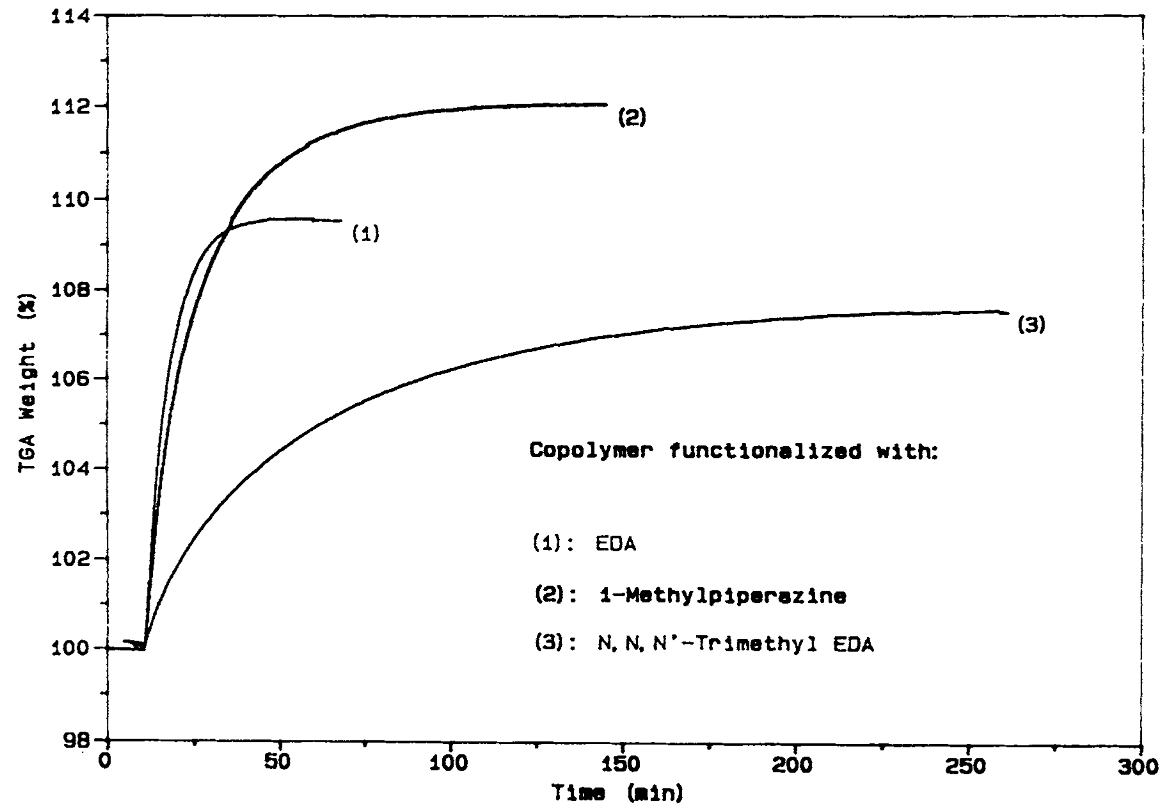


Figure 16 NO_2 sorption isotherms of amino-functional copolymers.

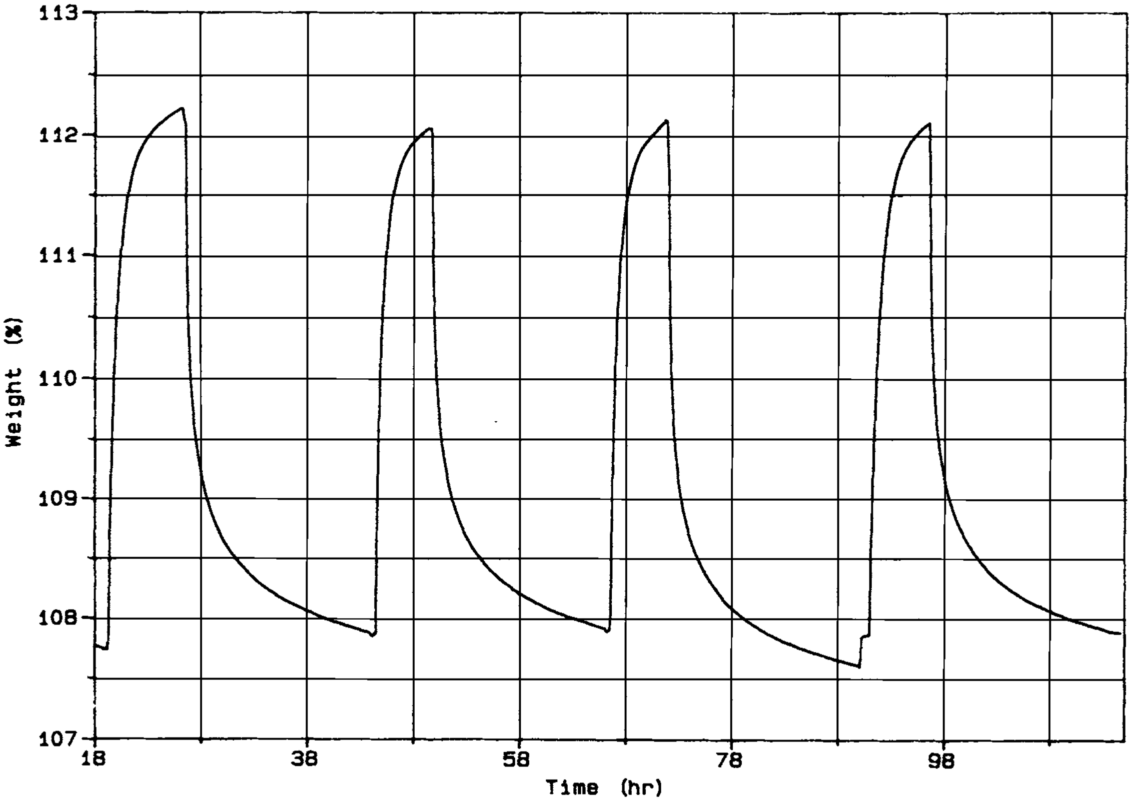


Figure 17 Cyclic NO_2 sorption/desorption using a thiomorpholine-functional copolymer.

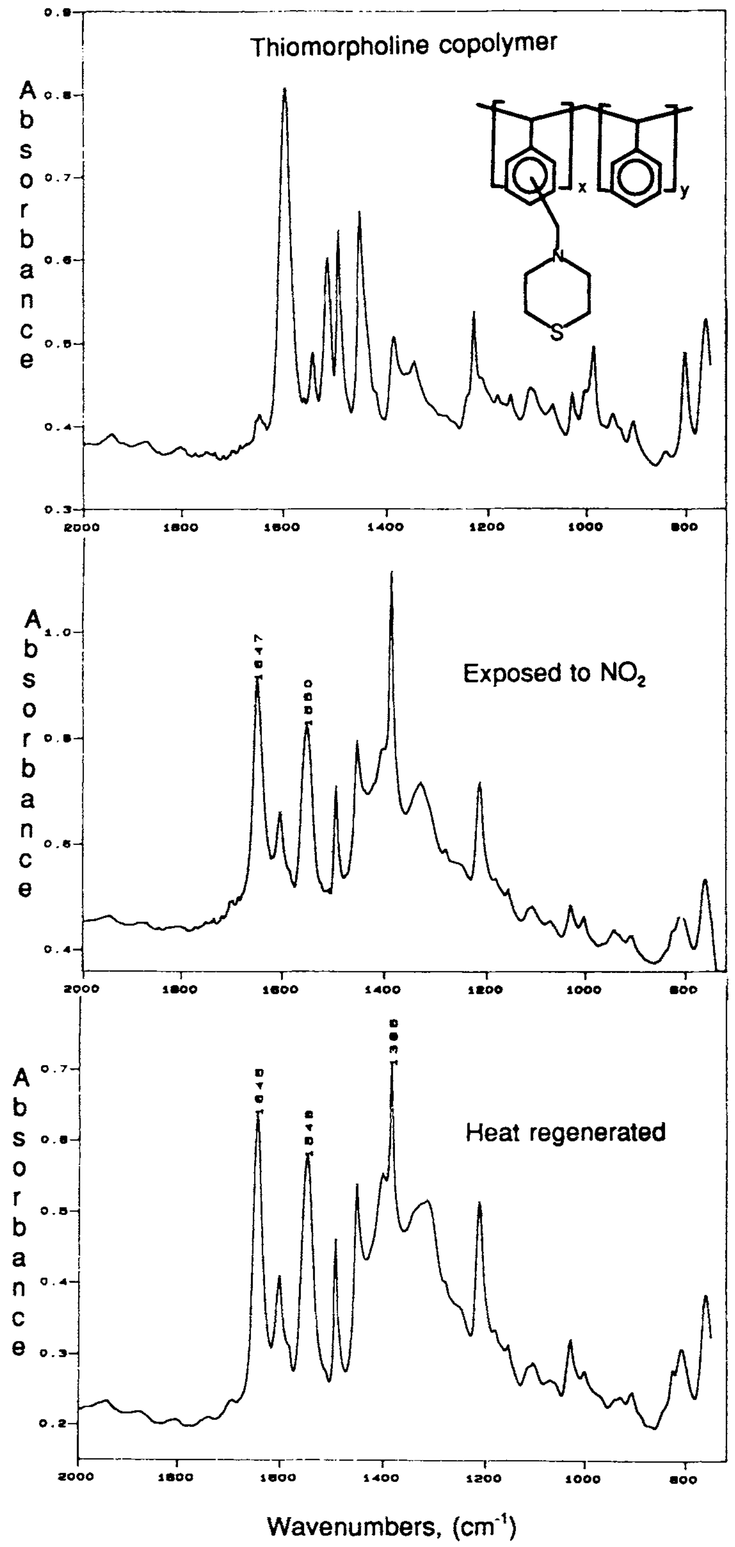


Figure 18 FTIR spectra of linear copolymer functionalized with thiomorpholine (upper curve), exposed to NO_2 (middle), and after heat-regeneration (lower curve).

lose up to 80% of their NO-sorption capacity after the first exposure to the gas due, presumably, to oxidation of the accessible amine active sites. The FTIR spectra (Fig. 15) of the heat-regenerated samples revealed degradation of the active sites as evidenced by the appearance of two bands at 1630–1700 and 1385 cm^{-1}, consistent with the formation of nitrite and nitroso groups, respectively, as reported in previous work by Drago and Paulik.[9]

In the case of NO_2, the TGA experiments showed that both the linear and the cross-linked sorbents have a high affinity for the gas as evidenced by a rapid rate of reaction and a high NO_2 sorption capacity (Fig. 16). On the average, the EDA, 1-MPip, and *N,N,N'*-TMEDA linear copolymers bind 0.55, 0.75, and 0.47 NO_2 molecules per nitrogen, respectively. FTIR spectra of the sorbents (with primary, secondary, and tertiary amines) before and after regeneration consistently revealed vibrational bands at 1385 and 1600–1700, again indicative of oxidation products. Reference runs with PS and a S–VBC copolymer showed that neither NO nor NO_2 are absorbed by these materials.

In view of the well-known fact that NO_2 can act both as an electron donor and an acceptor, our preliminary TGA results (Fig. 17) using functional polymers with dual weak donor and acceptor properties showed that styrenic copolymers carrying pendant groups such as thiomorpholine proved to be potential organic-based materials for the reversible absorption of NO_2. Although the chemical identity of the addition products is not yet fully elucidated, FTIR spectra (Fig. 18) of the virgin copolymer, and a sample subjected to several cyclic exposures to NO_2 before and after heat regeneration, showed the familiar absorption bands emanating from NO_2/tertiary amine oxidation products (1650 and 1385 cm^{-1}). The presence of an additional strong band at 1550 cm^{-1} for the exposed sample before and after regeneration, consistent with the vibrational band of a nitro compound, is still enigmatic at this point as to its chemical origin.

CONCLUSIONS

Cross-linked EDA-functional, S–DVB-based polymer networks were found to exhibit high affinity and selectivity for the reversible sorption–desorption of acidic gaseous substrates. Their sorption capacity was found to be superior to their linear counterparts, presumably owing to a higher surface concentration and better accessibility of the amine active sites, viz., more favorable diffusion conditions.

Although tertiary amine-functional copolymers exhibit a rather poor CO_2-sorption capacity, they were found to have a high affinity for Lewis acid gases stronger than CO_2 (SO_2, for instance). These materials are capable of readily forming amine : SO_2 adducts that dissociate cleanly following a mild heat treatment, thus resulting in the regeneration of the polymeric sorbent. EDA-functional polymers were found to have a higher sorption capacity for SO_2 than that of the tertiary amino-functional sorbents, owing presumably to their stronger Lewis basicity. The SO_2/primary amine adducts were found to dissociate slowly and nearly completely under nitrogen at ambient conditions.

NO_2 was the most strongly absorbed substrate by the amino-functional polymers. Oxidation of the active sites remains the major obstacle for the condition of thermal reversibility for both NO and NO_2 absorption. Ongoing research in our laboratory shows that thiomorpholine-functional copolymers absorb NO_2 reversibly.

The authors wish to thank the National Science Foundation (CTS-9005155) and the Petroleum Research Fund (22901-G7) for financial support for this research.

REFERENCES

1. M. Fileti and A. Puccini, *Chem. Ber.*, **12,** 1308 (1879).
2. W. Siefken, *Annals,* **96,** 562 (1948).
3. J. F. Mulvaney and R. L. Evans, *Ind. Eng. Chem.*, **40,** 393 (1948).
4. H. Hikita, S. Asai, I. Ishikawa, and M. Honda, *Chem. Eng. J.*, **13,** 7 (1977).
5. S. S. Laddha and P. V. Danckwerts, *Chem. Eng. J.*, **36,** 479 (1981).
6. F. J. B. Garcia, *Ing. Quim.*, **Oct.,** 317 (1989).
7. J. L. Sotelo, F. J. Benitez, J. Beltran-Heredia, and C. Rodriguez, *Anal. Quim.*, **87,** 206 (1990).
8. M. Caplow, *J. Am. Chem. Soc.*, **90,** 6795 (1968).
9. R. S. Drago and F. E. Paulik, *J. Am. Chem. Soc.*, **82,** 96 (1960).
10. R. S. Drago and B. R. Karstetter, *J. Am. Chem. Soc.*, **83,** 1819 (1961).
11. A. Diaf and E. J. Beckman, *ACS Polym. Prepr.*, **33**(1), 956 (1992).
12. A. Diaf, R. M. Enick, and E. J. Beckman, *J. Appl. Polym. Sci.*, to appear.
13. A. Diaf and E. J. Beckman, in *1992 Annual AIChE Meeting,* Miami, FL., Nov. 1992, Paper 182g.
14. T. Tsuda, T. Fujiwara, Y. Taketani, and T. Saegusa, *Chem. Lett.*, **11,** 2161 (1992).
15. T. Tsuda and T. Fujiwara, *J. Chem. Soc. Chem. Commun.*, **22,** 1659 (1992).

16. D. C. Sherington, in *Encyclopedia of Polymer Science and Engineering,* 2nd ed., Wiley, New York, 1988, Vol. 14, p. 101.
17. J. O. E. Otaigbe, R. E. Banks, and S. Smith, *Br. Polym. J.,* **20,** 53 (1988).
18. J. M. J. Frechet, G. D. Darling, S. Itsuno, P. Z. Lu, M. V. de Meftahi, and W. A. Rolls, Jr., *Pure Appl. Chem.,* **60**(3), 353 (1988).
19. A. Guyot and M. Bartholin, *Prog. Polym. Sci.,* **8,** 277 (1982).
20. S. Kondo, T. Ohtsuka, K. Ogura, and K. Tsuda, *J. Macromol. Sci. Chem.,* **13,** 767 (1979).
21. D. Braun, W. Czerwinski, G. Disselhoff, F. Tudos, T. Kellen, and B. Turcsanyi, *Angew. Makromol. Chem.,* **125,** 161 (1984).
22. R. H. Wiley and E. E. Sale, *J. Polym. Sci.,* **42,** 497 (1960).
23. J. Malinski, J. Klaban, and K. Dusek, *J. Macromol. Sci. Chem.,* **A5,** 1071 (1971).
24. P. V. Danckwerts and M. M. Sharma, *Chem. Eng.,* **Oct.,** CE244 (1966).
25. P. Souchay and G. Pannetier, *Chemical Kinetics,* Elsevier, New York, 1967.
26. R. S. Drago, R. O. Ragsdale, and D. P. Eyman, *J. Am. Chem. Soc.,* **83,** 4337 (1961).
27. R. O. Ragsdale, B. R. Karstetter, and R. S. Drago, *Inorg. Chem.,* **4,** 420 (1965).

Received October 14, 1993
Accepted November 7, 1993