

# Molecular Redesign of Expanded Polystyrene to Allow Use of Carbon Dioxide as a Foaming Agent.

## I. Reversible Binding of CO<sub>2</sub>

A. DIAF, R. M. ENICK, and E. J. BECKMAN\*

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

### SYNOPSIS

Environmental concerns, associated with the production of expanded plastics using hydrocarbon blowing agents, have spurred interest in environmentally-friendly technology by which cellular materials, particularly expanded polystyrene, can be produced. Consequently, we have explored the possibility of using styrene-based, amino-functional copolymers to generate expandable systems, which would rely solely on CO<sub>2</sub> as a blowing agent. Carbon dioxide is an attractive foaming agent in that it can be readily extracted from the air, is nonflammable, and exhibits low toxicity. Using a styrenic copolymer, functionalized with ethylenediamine (EDA), the results of this study show that aminated polymers are capable of reversibly binding weakly acidic gases, CO<sub>2</sub> in particular. While the reaction products (polymer-bound zwitterions) are stable under ambient conditions, decarboxylation can be thermally induced cleanly and easily. Work underway in our laboratory shows that microporous, as well as nonporous EDA-functional copolymers, are effective, thermally-reversible sorbents for acid gases. Furthermore, preliminary results show that these materials may also find potential applications in facilitated transport membrane technology. © 1993 John Wiley & Sons, Inc.

### INTRODUCTION

The advent of cellular plastics has resulted in the emergence of a new class of structural materials with unique physico-mechanical properties. While the practical significance of these materials in today's specialized marketplace is unquestioned, the technology currently in use to produce expanded products suffers from major drawbacks, namely, the release of ozone-depleting and greenhouse gases into the atmosphere.

Because of a greater awareness concerning global air pollution, our goal is to conceive a process by which cellular plastics can be made in compliance with the most stringent environmental protection regulations. This work attempts to contribute to the elaboration of a "clean" foaming process, based solely on carbon dioxide as a foaming agent, thus completely eliminating the use of hydrocarbons or chlorofluorocarbons as blowing agents.

The technique consists of developing modified polystyrenes, containing pendant functional groups that are capable of reversibly associating or reacting with CO<sub>2</sub>. Previous work<sup>1-4</sup> has shown that primary or secondary amines react readily with carbon dioxide to form products whose thermal stability is a function of the amine structure and its  $pK_b$ .<sup>5</sup> Upon heating, these materials will revert to free amine and carbon dioxide.<sup>6,7</sup>

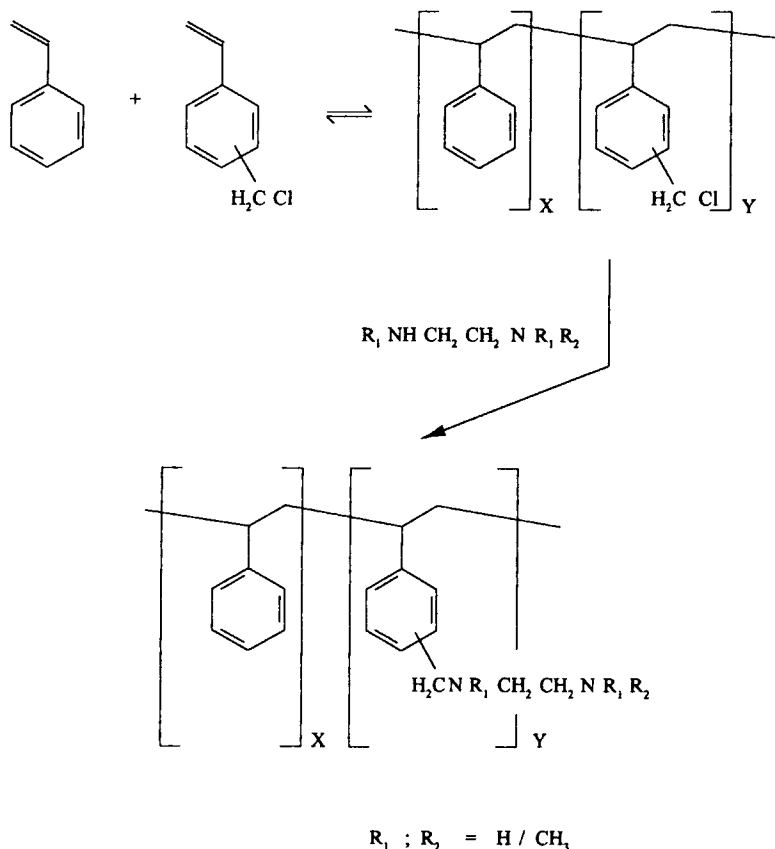
Although there are many ways by which amino-functional polymers can be prepared, the amino copolymers evaluated for the purpose of this study are synthesized via a postpolymerization modification of a styrene-*co*-vinylbenzylchloride (S-VBC) copolymer precursor, according to the scheme shown in Figure 1.

### EXPERIMENTAL

#### Synthesis of S-VBC Copolymers

Styrene and VBC (70% meta, 30% para), from Aldrich, are washed separately with a 0.5% aqueous so-

\* To whom correspondence should be addressed.



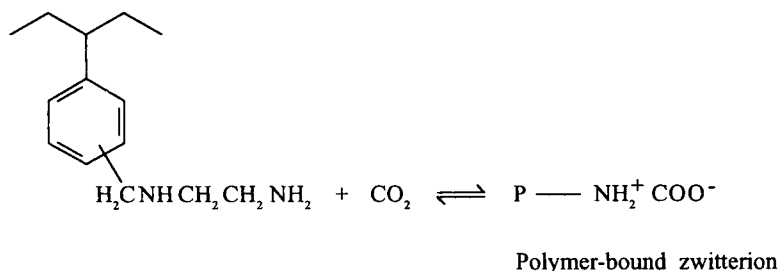
**Figure 1** Scheme for synthesis of amino-functional styrene copolymers.

dium hydroxide solution to remove the polymerization inhibitors. This process is repeated for a minimum of three times. The monomers are then rinsed with distilled water for at least six times to eliminate all traces of the sodium hydroxide. Molecular sieves are added to the monomers, which are then stored for a minimum of 24 h in a refrigerator at 4°C. Monomers are then distilled under vacuum prior to polymerization.

The precursor copolymers are made in a toluene (Fisher) solution, via free radical polymerization, initiated by azo-bis-isobutyronitrile (AIBN) (Aldrich). Typically, a 3000 mL, three necked, round bottomed flask, mounted with a reflux condenser, is flushed with nitrogen for 1 h. The reactor is 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 is stirred at room temperature for 30 min while bubbling nitrogen into the reactants. The nitrogen feed is then shut off and the reactor is immersed in an oil bath, preheated to 105°C, and the contents are

stirred overnight. The copolymer is recovered by pouring the solution into a large volume (100 mL) of methanol (Fisher). The precipitate is separated by filtration, redissolved in chloroform (Fisher), and coagulated again in methanol. The product is finally washed several times with small volumes (50 mL) of methanol and is dried under vacuum.

Copolymer composition was determined by elemental analysis at Galbraith Laboratories, Knoxville, Tennessee, and also via high resolution proton-NMR (Bruker MSL300 instrument with a 5-mm high resolution probe and deuteriochloroform as a solvent). In the case of the proton-NMR analysis, copolymer composition is calculated from the relative intensities of the chloromethyl proton signal. 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 ( $M_w$ ) and polydispersities were found to range from 98,000 to 130,000 and 2.5 to 3.2, respectively. Glass transition



**Figure 2** Reaction of CO<sub>2</sub> with amino-polymers.

temperatures ( $T_g$ ) were evaluated with the 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.

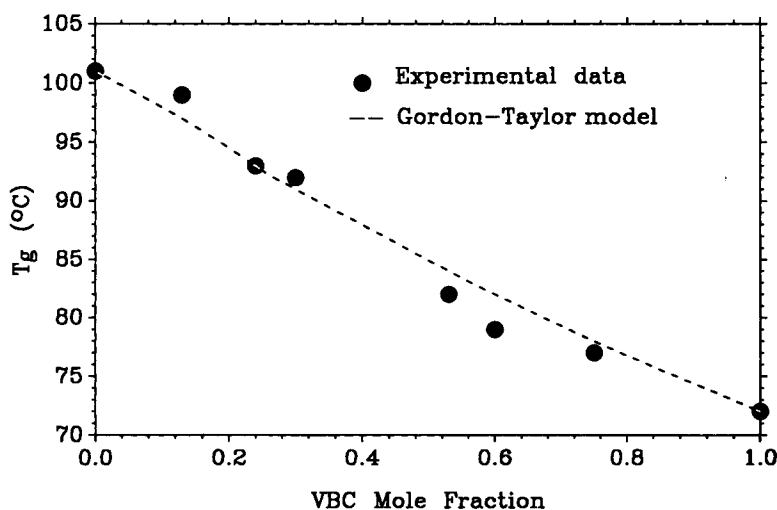
### Preparation of Amino-Polymers

The alkylation reactions, to produce aminated copolymers, are performed in a toluene solution at 30°C, under nitrogen atmosphere, in the presence of a polymer-supported dialkylaminopyridine catalyst (PolyDMAP, Reillex Industries). In a typical experiment, 5.259 g of an S-VBC copolymer (with a 30% VBC molar content) are dissolved in 150 mL of toluene. Meanwhile, 8.92 g (149 mmol) of EDA (Aldrich) (large excess of EDA to VBC) and 20 mL of toluene are placed in a 3000 mL, three necked, round bottomed flask, previously flushed with nitrogen as indicated in the preceding section. The copolymer solution is added dropwise into the amine

solution while stirring vigorously. The mixture is stirred for 3 days, heated to 90°C for 4 h, is then poured into 1500 mL of a 5% aqueous sodium hydroxide solution, and is stirred at room temperature overnight. To recover the copolymer, the solvent is evaporated under vacuum and the water insoluble fraction of the amino copolymer is separated by filtration, is washed thoroughly with distilled water, and then is dried under vacuum. The preparation of materials, functionalized with other ethylenediamine variants, was also accomplished following these procedures.

### Binding of Carbon Dioxide by Amino Polymers

Styrene-based copolymers, functionalized with EDA, react readily with carbon dioxide to form polymer-bound zwitterions, as shown schematically in Figure 2. These reactions were conducted either in bulk or in solution as follows:



**Figure 3** Glass transition of styrene/vinylbenzylchloride (S-VBC) copolymers.

1. Copolymer powder or a compression molded disk or film (13 mm in diameter) is exposed to carbon dioxide at ambient temperature and pressure, at the vapor pressure, or at supercritical conditions.
2. The aminated copolymer is dissolved in chloroform under ambient conditions. Upon sparging with CO<sub>2</sub>, a white precipitate quickly appears, indicating the formation of the polymer-bound zwitterion. The product is separated by filtration and is dried under vacuum.

The amount of carbon dioxide, fixed by the aminated copolymers upon exposure to the gas, is measured by thermogravimetric analysis (TGA), using a 0.100 mL platinum pan, and operated at a heating rate of 10°C/min, using a nitrogen gas purge at 50 mL/minute through the balance and furnace compartments.

The chemical composition of the gases evolved upon heating is determined by mass spectroscopy, using the Dycor quadrupole instrument. After exposing an amino-copolymer in the bulk state to CO<sub>2</sub> at its vapor pressure, the product of the reaction is sealed in a vial under a nitrogen atmosphere. Mass spectroscopy data are collected by first sampling the ambient air for 1 min. Immediately thereafter, the sampling capillary is inserted into the vial and the gases inside the vial are analyzed at ambient temperature for 1 min. Finally, the vial is immersed in an oil bath preheated to 90°C and data are taken for another 15 min. In the course of this experiment, the instrument is set to monitor carbon dioxide, water, and nitrogen.

Fourier transform infrared spectroscopy (Mattson Polaris) was used to probe for functional groups present at various stages of the CO<sub>2</sub> fix-release cycle. Samples for the FTIR experiments were prepared in the form of thin films, cast from a solution of the aminated copolymer in chloroform. The FTIR spectra of virgin film, and those exposed to liquid CO<sub>2</sub> for several hours, are recorded. The exposed sample is then heated to 80°C for 5 min in a vacuum oven and its FTIR spectrum is recorded again.

## RESULTS AND DISCUSSION

### Styrene-co-Vinylbenzylchloride Copolymers

The reactivity ratios reported in the literature,<sup>8,9</sup> for a styrene-VBC system, suggest that copolymeriza-

tion of these monomers would probably proceed to yield random copolymers. Differential scanning calorimetry (DSC) measurements revealed the presence of only one single glass transition temperature, indicating that these precursors are indeed predominantly of the random type within the sensitivity limits of the thermal analysis technique to fine structure. The glass transition temperatures of the precursors were found to vary with copolymer com-

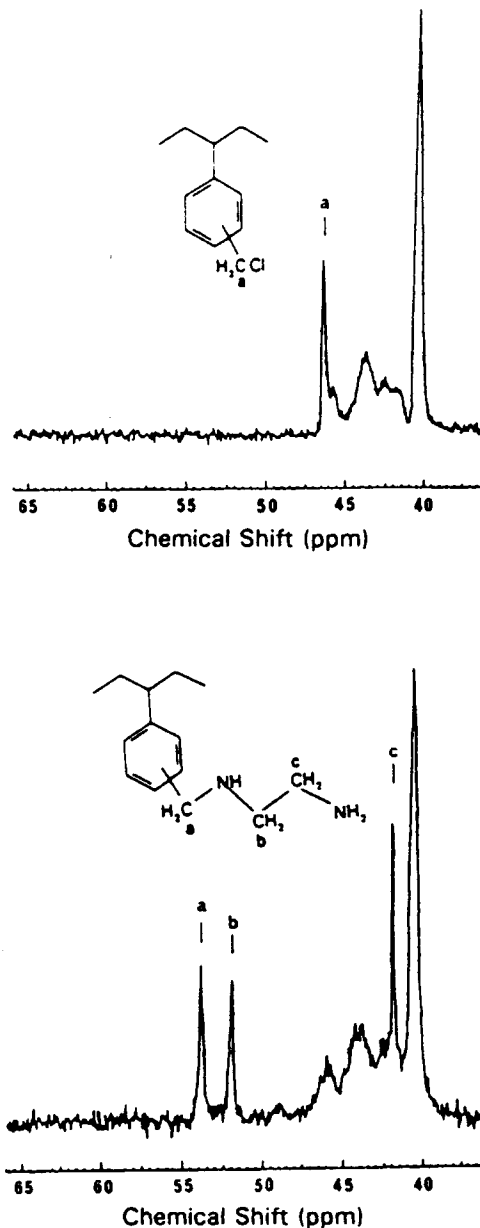


Figure 4 <sup>13</sup>C-NMR spectra of S-VBC and EDA-functional copolymers.

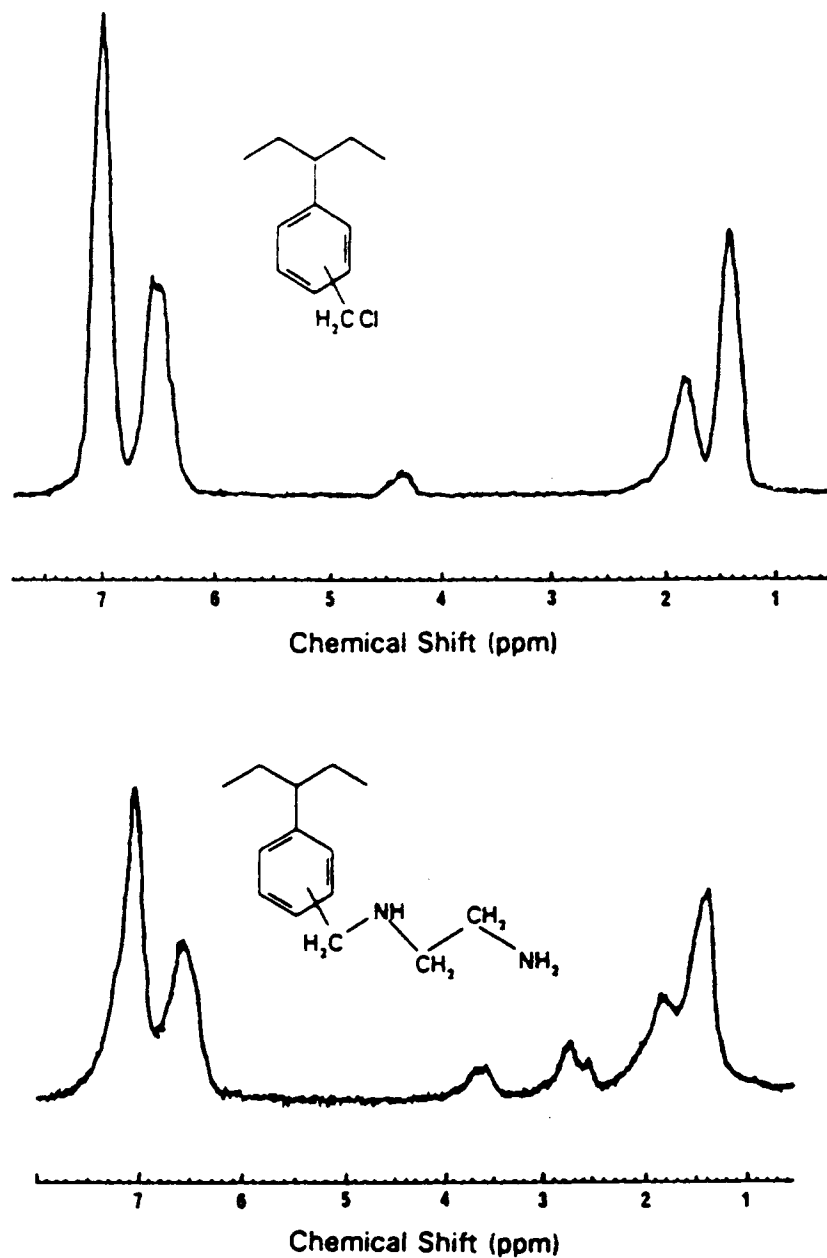


Figure 5 <sup>1</sup>H-NMR spectra of S-VBC and EDA-functional copolymers.

position, as shown in Figure 3. The empirical model, developed by Gordon and Taylor,<sup>10</sup> for the prediction of the glass transition temperature of random amorphous copolymers, fits well the experimental data, using  $k = 0.74$ .

#### Amino-Functional Copolymers

Evidence for the formation of the amino-copolymer is provided by elemental analysis and <sup>13</sup>C-NMR. For

example, the spectra shown in Figure 4 indicate that the alkylation reaction is quantitative. The proton-NMR spectra, reported in Figure 5, also support this conclusion. 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 6. As is shown in Figure 6, low amounts of EDA-functional comonomer act to plasticize the polymer, lowering  $T_g$  from 101°C (styrene homopolymer) to 80°C at

**Table I** Glass Transition Temperatures of Amine-Copolymers as a Function of Structure and Composition

Amine Type	Structure	Mole Fraction	
		0.13	0.24
EDA	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$	101	92
N-MEDA	$\text{HNCH}_3(\text{CH}_2)_2\text{NH}_2$	84	90
N,N-DMEDA	$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{N}(\text{CH}_2)_2\text{NH}_2 \\ \diagup \\ \text{H}_3\text{C} \end{array}$	103	91
N,N'-DMEDA	$\text{H}_3\text{CNH}(\text{CH}_2)_2\text{NHCH}_3$	101	79
N,N,N'-TMEDA	$\begin{array}{c} \text{H}_3\text{C} \\ \diagdown \\ \text{N}(\text{CH}_2)_2\text{NHCH}_3 \\ \diagup \\ \text{H}_3\text{C} \end{array}$	97	94
TETA	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$	—	70

40 mol %, the further addition of EDA-functional comonomer dramatically increases  $T_g$ , such that a 50/50 copolymer exhibits a  $T_g$  of 103°C and copolymers, with high functional comonomer content (60, 75, and 100%), did not show any thermal transition within the range of -60 to 300°C. These polymers are readily soluble in chloroform/methanol mixtures; thus it is not likely that crosslinking has produced this anomalous  $T_g$  behavior. At this point, this unusual behavior may be rationalized by the formation of strong electronic interactions between

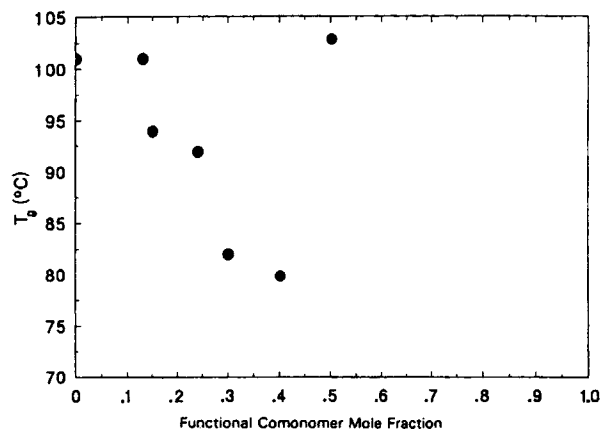
the phenyl groups and the unshared nitrogen doublet at high amine content, resulting in severe hindrance of segmental mobility. TGA measurements revealed that these materials undergo no weight loss up to 300°C, indicating a thermal stability comparable to that of a styrene homopolymer.

#### Cyclic Reactions of Amino-Copolymers with CO<sub>2</sub>

Following exposure to carbon dioxide, amino-functional polymers were allowed to age at atmospheric conditions for 24 h prior to the TGA experiments. Typical CO<sub>2</sub> desorption curves, recorded by DSC and TGA, are shown in Figure 7. As can be seen, the weight loss due to CO<sub>2</sub> release occurs abruptly, and is completed relatively quickly. The nonlinear dependency of adsorbed CO<sub>2</sub> weight fraction (Fig. 8) and amine content is believed to be due to CO<sub>2</sub> diffusion limitations, poorer solubility of the copolymer at higher amine loadings, and the inaccessibility of amine sites entrapped in the bulk of the precipitate during the reaction with CO<sub>2</sub>.

The amount of carbon dioxide bound by these copolymers is a function of amine structure, as shown in Table II. These data suggest the following generalizations:

1. Binding capacity of pendant amine groups increases as amine basicity (relative to a

**Figure 6** Glass transition of EDA-functional copolymers.

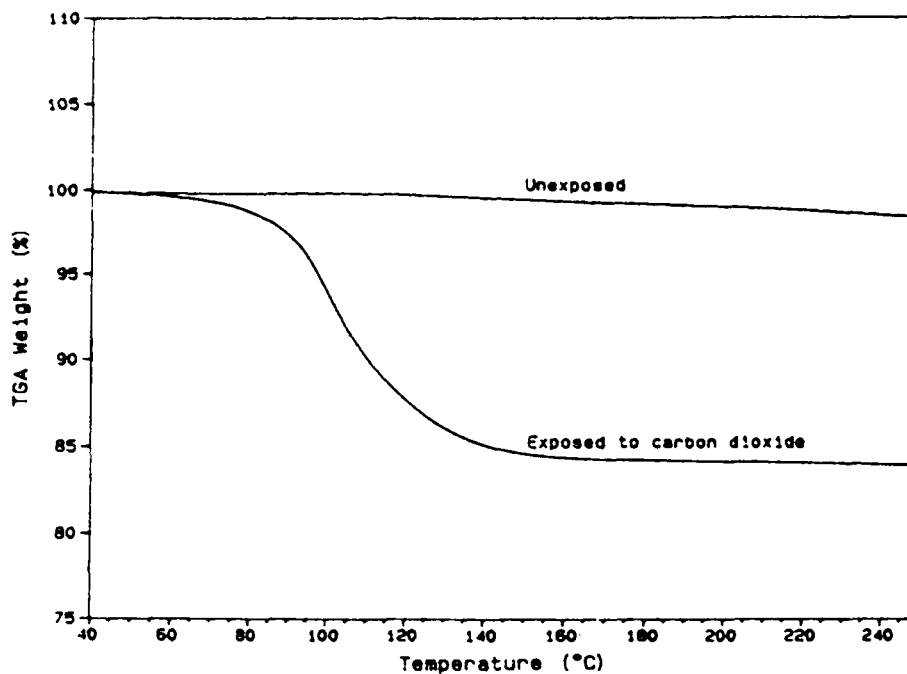
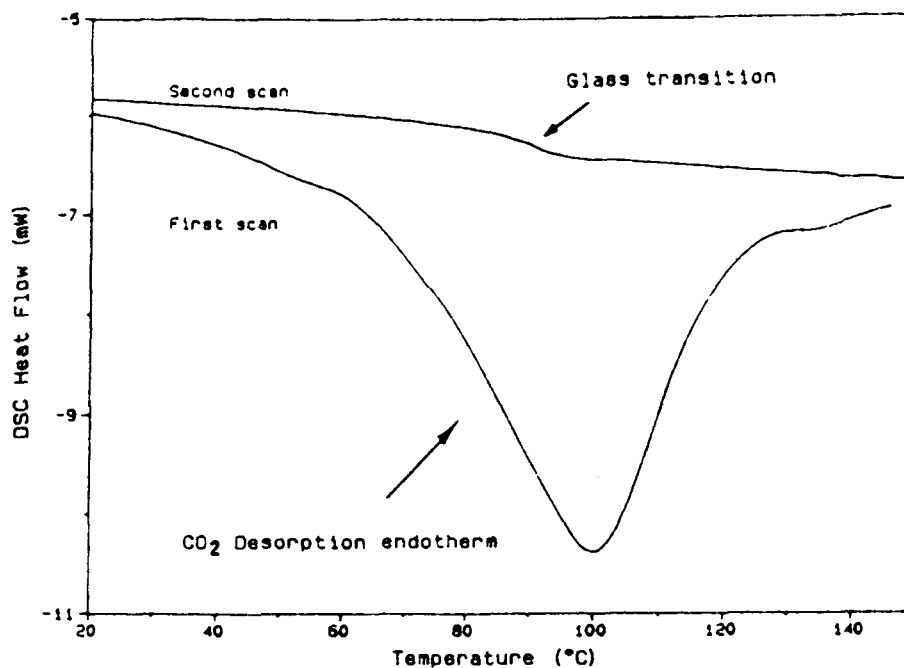
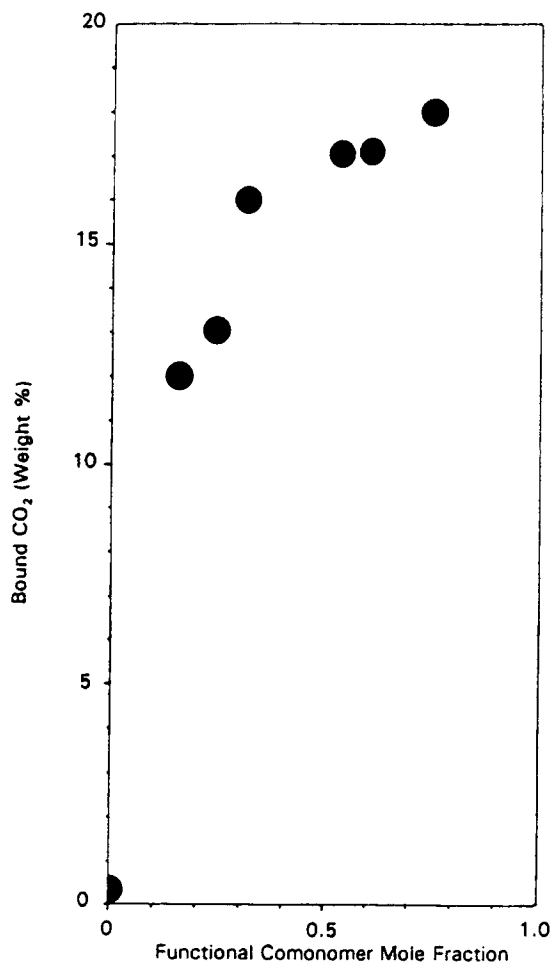


Figure 7 TGA scan of CO<sub>2</sub> release by EDA-copolymer/CO<sub>2</sub> reaction products.

- Lewis acid, such as CO<sub>2</sub>) increases, that is, primary > secondary > tertiary.
- Thermal stability of amine-CO<sub>2</sub> adducts appears to increase upon attachment of the

amine to the polymer backbone, in that a tertiary amine-functional polymer binds CO<sub>2</sub> (albeit a small amount), whereas a low molecular weight tertiary amine does not.



**Figure 8** CO<sub>2</sub> capacity of EDA-functional copolymer vs. EDA content.

- Placement of the amine groups (relative to the phenyl groups) has little or no effect on the CO<sub>2</sub>-binding capacity (compare results for N,N-DMEDA [secondary-tertiary] and N,N'-DMEDA [tertiary-secondary]).

As shown by the TGA and DSC scans, the onset of catastrophic thermal dissociation occurs at 70°C and is complete at 160°C (at ambient pressure). Using a high pressure DSC cell, the CO<sub>2</sub> desorption endotherm is shifted to higher temperatures when the test pressure is increased, as shown in Figure 9. Visual, as well as microscopic, examination of the sample residues revealed that these products exhibit a foamed structure.

Mass spectroscopy experiments, in parallel with FTIR spectroscopy, proved to be a useful combination for the characterization of the reaction prod-

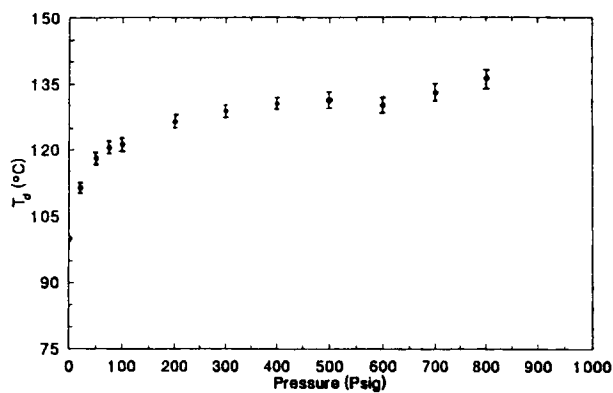
**Table II** CO<sub>2</sub> Binding as a Function of Amine Structure and Reaction Conditions

Amine Type	Bound CO <sub>2</sub> Wt %	
	Method A <sup>a</sup>	Method B <sup>b</sup>
EDA	3.8	13
N-MEDA	1.7	5.6
N,N-DMEDA	1.9	4.2
N,N'-DMEDA	1.0	4.0
N,N,N'-TMEDA	1.1	1.8
Polystyrene Homopolymer	<0.1	

<sup>a</sup> Amino-copolymer exposed to liquid CO<sub>2</sub> at its vapor pressure.

<sup>b</sup> Amino-copolymer exposed to CO<sub>2</sub> at 1 atmosphere in chloroform solution.

ucts and also for the investigation of possible side-reactions (potential for urea formation<sup>11</sup>). Typical spectra (Fig. 10) do not exhibit absorption bands characteristic of urea functionalities (at 1650 cm<sup>-1</sup> in the case of diethylurea), suggesting that the decarboxylation step results in a clean regeneration of the original aminated copolymer. Further evidence in support of this observation is provided by the mass spectroscopy data, presented in Figure 11. Upon heating the CO<sub>2</sub>/EDA-copolymer reaction products, the carbon dioxide signal increased by several orders of magnitude, whereas the water signal remained unchanged throughout the course of the experiment. In addition, cyclic reactions of adsorption vs. thermally induced desorption of CO<sub>2</sub> are fully reproducible, proving that the process of reacting and regenerating the amino sites proceeds cleanly.



**Figure 9** Desorption onset temperature ( $T_d$ ) vs. CO<sub>2</sub> pressure.



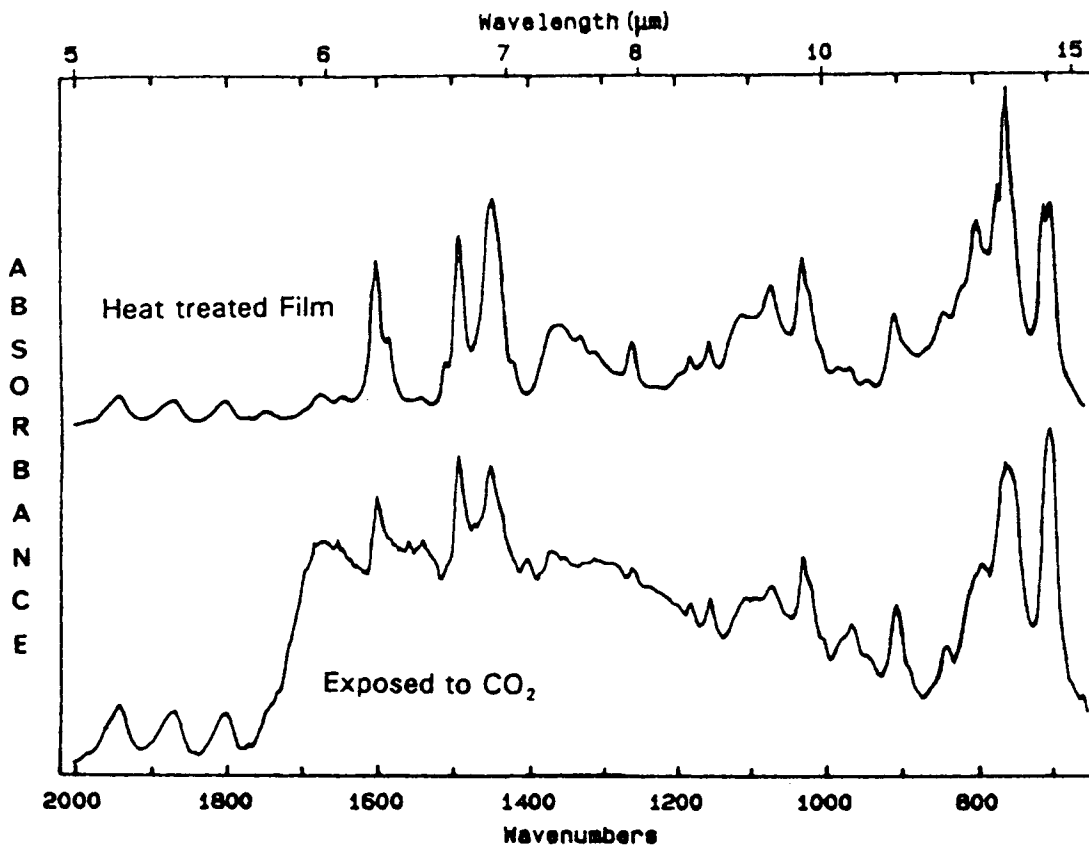


Figure 10 FTIR spectra of EDA-functional copolymer: upper curve is film following CO<sub>2</sub> exposure and subsequent heat treatment, lower curve is film after CO<sub>2</sub> exposure alone.

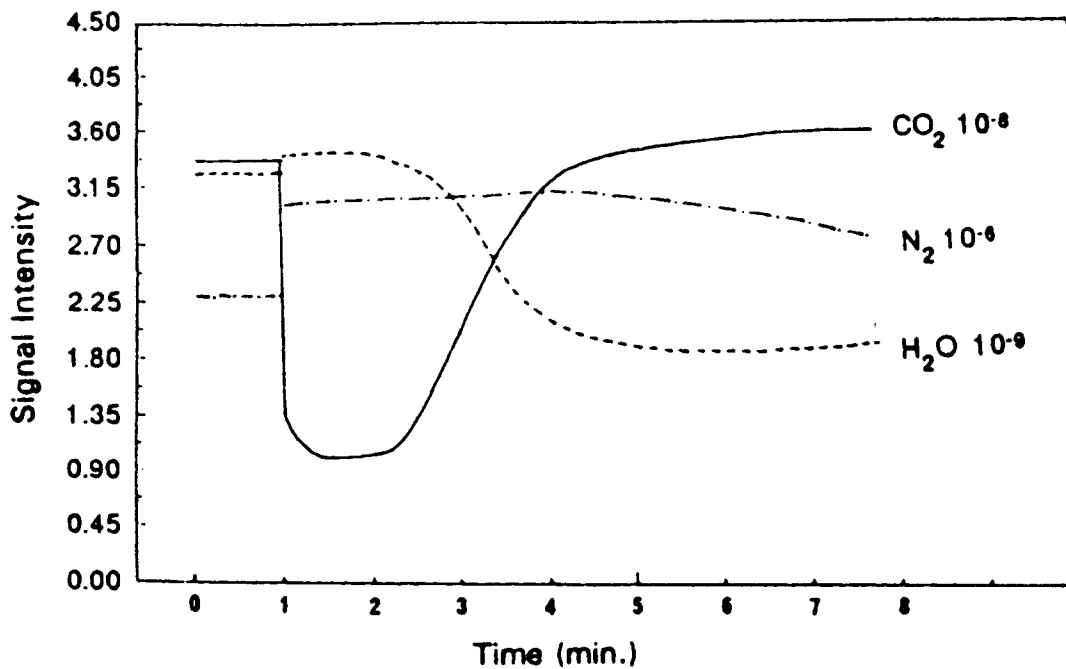


Figure 11 Mass spectroscopy data, collected during thermally-initiated release of CO<sub>2</sub> from EDA-copolymer/CO<sub>2</sub> reaction product.

## CONCLUSIONS

EDA-copolymers were found to react readily with CO<sub>2</sub> under a variety of conditions, including absorption of CO<sub>2</sub> from the air at ambient conditions. Thermal dissociation of the adsorbed CO<sub>2</sub> occurs in a clean fashion, resulting in the regeneration of the original aminated copolymer. The binding capacity of the pendant amine groups increases in the order primary > secondary > tertiary, following increases in relative basicity. Remarkably, the thermal stability of amine/CO<sub>2</sub> adducts increases when the amine is coupled to the polymer backbone, as made evident by our observation that a tertiary amine-functional polymer actually binds CO<sub>2</sub>.

Work<sup>12</sup> underway in our laboratory shows that microporous, as well as nonporous, EDA-functional copolymers are effective, thermally-reversible sorbents for acid gases.

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, *Ber*, **12**, 1308 (1879).
2. F. J. B. G. Javier, *Ing. Quim.*, **Oct.**, 317 (1989).
3. S. S. Laddha and P. V. Danckwerts, *Chem. Eng. Sci.*, **37**, 475 (1982).
4. G. F. Versteeg and W. P. M. Swaaij, *Chem. Eng. Sci.*, **43**, 573 (1988).
5. D. K. Dandge, J. P. Heller, and K. V. Wilson, *IEC Prod. Res. Dev.*, **24**, 162 (1985).
6. L. E. Robb, U.S. Patent No. 3,029,227, April 10, 1962, assigned to Minnesota Mining and Manufacturing.
7. N. Brodoway, U.S. Patent No. 4,102,801, July 25, 1978, assigned to E.I. Dupont de Nemours & Co.
8. S. Kondo, T. Ohtsuka, K. Ogura, and K. Tsuda, *J. Macromol. Sci., Chem.*, **13**, 767 (1979).
9. D. Braun, W. Czerwinski, G. Disselhoff, F. Tudos, T. Kellen, and B. Turcsanyi, *Angew. Makromol. Chem.*, **125**, 161 (1984).
10. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
11. G. D. Buckley and N. H. Ray, U.S. Patent No. 2,550,767, May 1951, assigned to ICI Limited, Great Britain.
12. A. Diaf, J. L. Garcia, R. M. Enick, and E. J. Beckman, in preparation.

Received September 17, 1992

Accepted December 11, 1992