ELSEVIER
Reactive & Functional Polymers 39 (1999) 197–205
REACTIVE & FUNCTIONAL POLYMERS

1,2-Diaminoethane-containing epoxy resins for separation of aldehydes

Niyazi Biçak*, A. Bahattin Soydan, B. Filiz Şenkal, Güneş Koza, Mine Yener

Istanbul Technical University, Department of Chemistry, Maslak, 80626 Istanbul, Turkey

Received 8 May 1997; accepted 23 December 1997

Abstract

Epoxy-amine resin obtained by inverse suspension polycondensation of epichlorohydrin with ethylenediamine has been demonstrated to be very useful for selective separation of aldehydes from the mixtures. 1,2-Diamino ethane units in the crosslinked structure can be regard as polymeric analog of Wanzlick reagent (1,2-dianilo ethane) which readily condenses with aldehydes to form five-membered cyclic structures, imidazolines. In the presence of mineral acids the imidazoline ring decomposes into its components. This reverse reaction serves a means of regenerability of the aldehyde loaded polymer. The method described in the present study is especially suitable for extraction and recovery of aromatic aldehydes from organic mixtures, even in small quantities.

The method works also for aliphatic aldehydes. However, in that case, aldol condensation products form in the solution and the insoluble polymer sorbs these by-products together with the aldehyde itself.

Aldehyde sorptions are rapid in water-miscible solvents such as dioxane and methanol. Whereas in cyclohexane aldehyde sorption is very slow, due to hydrophilicity of the polymer. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aldehyde separation; Epoxy-amine resin; Polymers with ethylenediamine

1. Introduction

Isolation of the products from the reaction mixtures is one of the most important steps of chemical processes. Polymer-supported extracting agents offer simplicity for isolation of one of the products from the reaction mixtures. Crosslinked polymers are preferred as support due to their insolubility. Because in that case isolation of one of the entities is reduced to a simple filtration. If the functional group attached to the crosslinked polymer is selective for a compound targeted, it will be possible to pick it up and separate easily from the mixtures.

In some aspects, polymeric protecting agents may also be considered as trapping agents. However, for the case of protection the aim is to protect any functional group of a compound for the next reaction. But in trapping, a polymeric reagent binds selectively one of the components of a reaction mixture. This phenomena has been termed as a ‘fishing out process’ [1]. In the literature, there are many reports on the use of polymeric protecting agents for alcohols [2], aldehydes [3] and carboxylic acids [4]. But, only few reports on polymeric trapping agents

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*Corresponding author.

PII: S1381-5148(98)00010-8

have been published so far. Polymer-supported semicarbazide has been demonstrated to be efficient for removal of small quantities of aldehydes by means of involvement of hydrazide groups [5]. But the regeneration of this polymeric extracting agent is not possible due to the hydrolysable hydrazide groups and the reagent described is not appropriate for recycling.

In a successful study, crosslinked polystyrene with diol residues has been used to isolate aldehydes and ketones in benzene solutions by reversible acetal or ketal formation [6]. Also *trans* and *cis* cyclohexanols have been separated by polymer-supported boronic acid based on selectivity of boron ester formation of the *cis* isomer [7].

Although this methodology is the key principle of affinity chromatography, so far no reports exist on the use of polymeric extracting agents for large scale separations; the subject remains to be developed.

The present work deals with separation of aldehydes by using epoxy-amine resins having 1,2-diamino ethane units in the main chain. Dianilino ethane, which is a so-called Wanzlick reagent, has been reported to form imidazolines with aldehydes [8]. This reaction has been reported to be reversible in acid conditions. Upon treating with dilute mineral acids, the imidazoline decomposes into its components. In this study, this analogy has been extended to polymeric 1,2-diamino ethanes. However, this process is not straightforward, because during decomposition of the imidazoline group with acids, side reactions always occur through phenyl rings, and these side reactions reduce the reactivity of dianilino ethane in subsequent uses. Similarly, in our laboratory we have observed that the crosslinked polymer obtained by condensation of *p*-dichloromethyl benzene and ethylenediamine also binds aldehydes. However, after the first regeneration by concentrated acids (i.e. 1 M) the reactivity of the polymeric reagent lowers to one-third of its original reactivity [9].

The change of the reactivity might be because of acid-catalyzed heterocondensation reaction (possibly Sommelet rearrangement) through amino group and phenyl ring.

In order to avoid this side reaction we have searched for a suitable polymer. We have concluded that the crosslinked epoxy-amine resin obtained by condensation of ethylene diamine with epichlorohydrin is suitable for aldehyde uptake from the mixtures. Not having aromatic groups, this polymer may be appropriate for avoiding side reactions in the regeneration step. In this work we have investigated aldehyde-binding ability and regeneration conditions of the crosslinked epoxy-amine polymer for different aldehydes.

2. Experimental

Carbonyl-free methanol was prepared from commercial methanol (E. Merck) as described in the literature [10]. Benzaldehyde (Merck), acetaldehyde (Merck), salicylaldehyde (Merck) and butyraldehyde (BDH) were distilled before use. All the other chemicals used were analytical-grade commercial products. They were used as supplied (epichlorohydrin (Fluka), ethylenediamine (Merck)).

2.1. Preparation of the epoxy-amine resin

Direct interaction of epichlorohydrin with ethylenediamine causes violent explosions. An insoluble resin was prepared safely by suspension–polycondensation methodology, according to the procedure described elsewhere [11]. Stoichiometrically 10% excess of epichlorohydrin was used to obtain solid and insoluble product.

2.2. Determination of the accessible amine content

Inevitably, some of the amino groups are embedded in the polymer matrix. So, only some parts of the secondary amines are accessible and susceptible to aldehyde binding. In order to estimate the maximum capacity of the resin, 0.5 g of the resin sample was contacted with 20 ml of 2 M HCl solution for 24 h. The mixture was filtered and 10 ml of filtrate was titrated conductimetrically with 0.1 M NaOH solution in order to find the excess of the HCl used. From these data the accessible amine content was calculated as 15.1 mmol g^{-1} resin, which is 88.1% of the total amine function.

2.3. Aldehyde loading capacity of the resin

To estimate aldehyde-binding capacities of the resin, 0.5 g of the resin sample was soaked into a 25-ml alcohol solution of 13.5 mmol aldehyde, which is about two-fold excess of the theoretical capacity. The mixtures were stirred for 3 h at room temperature. At the end of this period the mixtures were filtered, and 1-ml samples were taken from the filtrates and transferred quickly into volumetric flasks. The samples were diluted with the carbonyl-free methanol up to appropriate concentrations ($\sim 10^{-5}$ M).

The aldehyde concentrations were determined colorimetrically according to the procedure based on 2,4-dinitrophenyl hydrazine method yielding an absorbtion maxima around 480 nm [10]. The sorbed amounts were calculated by differentiating the initial and final aldehyde contents of the interacted solutions. The relevant data were tabulated in Table 1.

2.4. Aldehyde sorption kinetics of the resin

Simple batch kinetic experiments were performed as follows: to 50 ml of methanolic aldehyde solution (3×10^{-2} M), 0.5 g of resin sample was added and the mixture was stirred gently. Two-ml aliquots were taken from the mixture at appropriate time intervals. The sample solutions were transferred into volumetric flasks and diluted properly. Aldehyde concentrations were assayed colorimetrically. The sorbed amounts were calculated as described above. Time-dependent aldehyde sorptions were depicted as shown in Fig. 1. The sorption of the aldehydes studied (benzaldehyde, salicyl aldehyde, butyraldehyde and acetaldehyde) obeys second-order kinetics. By plotting $1/\beta$ vs. time (where β represents percentage of the unreacted aldehyde in solution) the rate constants were found from slopes of the linear graphs. The results obtained have been collected in Table 1. To investigate the solvent effect, the sorption kinetics of benzaldehyde were studied using three different solvents, methanol, dioxane and cyclohexane, under the same conditions. The comparative data are depicted in Fig. 2.

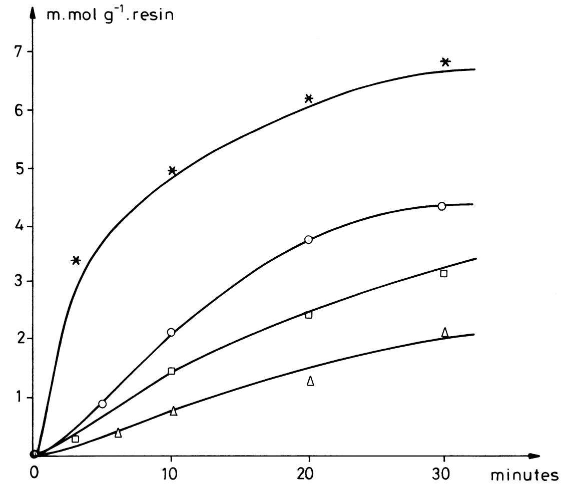


Fig. 1. Sorption kinetics of various aldehydes by the resin. Acetaldehyde (△), benzaldehyde (□), salicylaldehyde (○) and butyraldehyde (★).

2.5. Stripping of the aldehydes from the loaded resin

The desorption kinetics were studied by treating the aldehyde-loaded samples (0.5 g) with the mixture of 25 ml methanol (carbonyl-free) and 25 ml of 2 M HCl solutions. Time-dependent desorptions of benzaldehyde and butyraldehyde were followed by the samples taken at appropriate time intervals. For stripping of the aldehydes completely, the same experiments were repeated by prolonged interaction

Table 1
Aldehyde sorption charcteristics of the resin

Aldehyde	Loading capacity[a] (mmol g^{-1} resin)	Rate constant of sorption (mol^{-1} s^{-1} resin)	Percentage aldehyde released[b] (%)
Acetaldehyde[c]	3.94	8.1×10^{-3}	46.0
Butyraldehyde	6.60	1.94×10^{-2}	52.7
Benzaldehyde	5.66	1.63×10^{-2}	43.6
Salicylaldehyde	5.83	1.71×10^{-2}	67.6

[a] In 3 h.
[b] With 1 M HCl in 24 h.
[c] By negleting aldol products.

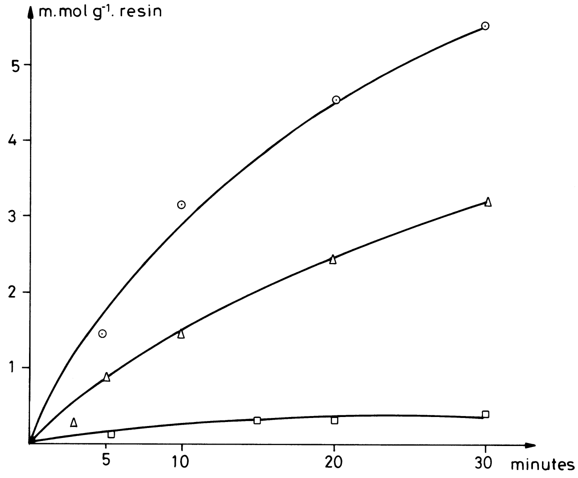


Fig. 2. Sorption kinetics of benzaldehyde in methanol (△), dioxane (⊙), cyclohexane (□).

periods (24 h) of the loaded samples with the acid solutions. The released aldehydes in the solutions were determined similarly.

2.6. Regeneration of the used resin

By treating with 1 M HCl solution only 43–67% of the sorbed aldehydes are released from the loaded samples. If, however, more concentrated (5 M) HCl solutions (25 ml/g of the resin) are used, the resin samples become completely aldehyde free in about 5 h. At the end of this procedure, the amino groups of the resin are in HCl form. In order to recover these samples, the washed samples were contacted with 25 ml of 2 M NaOH solutions. After washing with excess of water the regenerated samples were dried under vacuo at 40°C for 24 h.

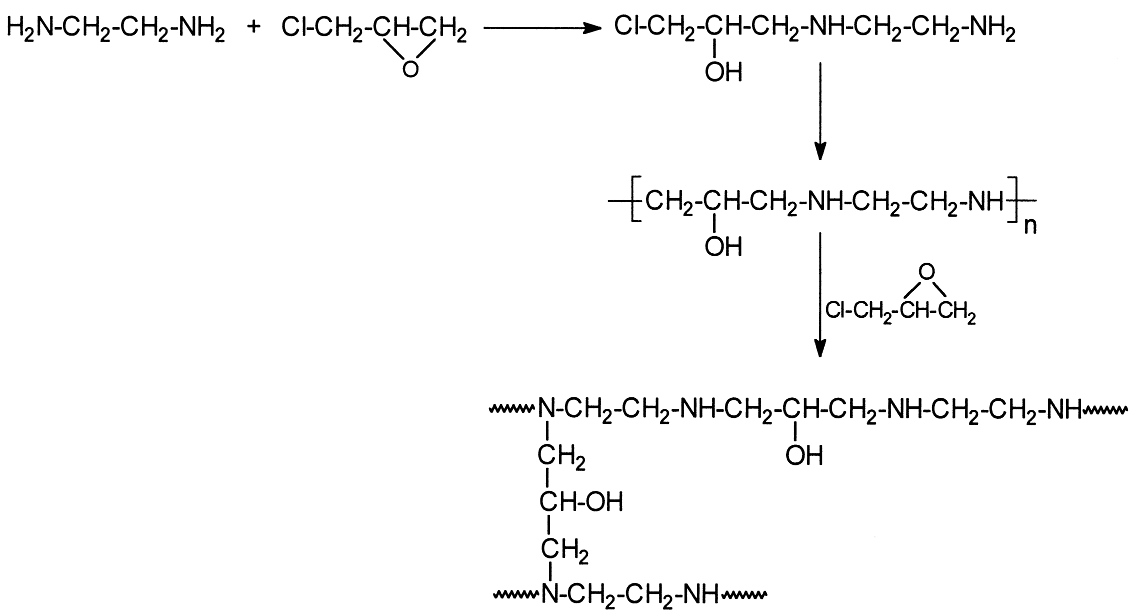
3. Results and discussion

The scope of the present work is to investigate the reversible aldehyde-binding ability of the crosslinked polymers with 1,2-diamino ethane units. In the study, the crosslinked insoluble polymer was obtained by condensation of the suspension of epichlorohydrin with ethylenediamine in liquid paraffin and its reversible aldehyde-binding ability was tested. The structure of the insoluble polymer is believed to be as shown in Scheme 1.

The excess of the epichlorohydrin might act as a crosslinking agent. According to this formula, the polymer does not contain primary amines, which seems to be unexpected for the condensation polymerization. In order to determine the primary amine content, we have used nitrous acid test, which is characteristic for primary amines. This method is known as Van-Slyke method which is used for quantitative determination of amino acids by measuring the volume of the nitrogen gas evolved from primary amino groups [12].

Interestingly, no nitrogen evolution was observed by nitrous acid test. This result clearly indicates that the insoluble epoxy-amine resin practically does not contain primary amino groups and the whole structure consists of secondary and tertiary amines as depicted in Scheme 1.

Since 10% excess of epichlorohydrin is used, theoretically secondary amino content of the crosslinked polymer is calculated as 15.51 mmol g^{-1} resin. But, in fact, some of the amines retain in the crosslinked structure and



Scheme 1.

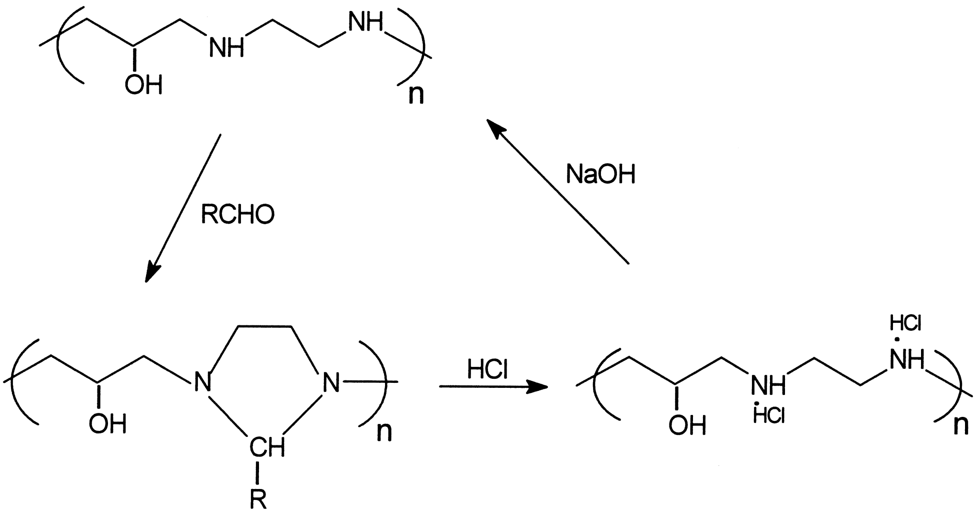
these are not accessible for chemical interactions. In order to estimate the accessible amine content a weighed amount of polymer sample was contacted with aqua solution of HCl (5 M) and the unreacted part of HCl in the test solution was determined by back-titration with 1 M NaOH solution. In this way the accessible amine content was calculated as 15.1 mmol g^{-1} resin. If we assume that secondary and tertiary amine distribution is equal in the accessible and inaccessible parts, 13.6 mmol of secondary amine must be as accessible. Since two amino groups are consumed per aldehyde molecule, the effective aldehyde-binding capacity of the polymer is expected to be 6.8 mmol g^{-1}.

3.1. Aldehyde sorption by the resin

Based on the reversible aldehyde-binding ability of dianilino ethane, aldehyde sorption of the polymer can be represented as shown in Scheme 2.

The aldehyde sorption must proceed via imidazoline ring formation. To break up the imidazoline moiety, concentrated HCl solution is used and the aldehyde sorbed is released from the polymer. This fact is the key point of the reversible aldehyde binding, which allows recovery of the sorbed aldehyde. After separation of the stripped aldehyde the amino groups in the polymer are in HCl form. These are readily converted into free amine form by a simple base treatment (1 M NaOH), and the crosslinked polymer becomes regenerated and ready for the subsequent use. In order to show practical efficiency of the resinous product, the resin samples were contacted separately with twofold excess of aldehydes for 3 h at room temperature. The loading capacities in this conditions were found by determination of the residual aldehyde concentrations of the solutions (Table 1). This inspection indicates that the loading capacity for butyraldehyde (6.6 mmol g^{-1}) is reasonably higher than those for the other aldehydes.

Having a low molecular weight, acetaldehyde is expected to show higher binding ability. However, in our conditions, we have observed that the resin itself acts as base catalyst for an aldol type of condensation of acetaldehyde, and the solution becomes red–brown on standing more than 4 h. This fact raises complications in



Scheme 2.

determining the aldehyde concentration. Aldol condensation is known to be a typical reaction of aliphatic aldehydes possessing α-hydrogen. Indeed the colored solution exhibits the characteristic odor of crotonaldehyde, which is the first condensation product of acetaldehyde.

During the sorption of acetaldehyde the resin also becomes colored. This can be ascribed to a fast aldol condensation of acetaldehyde and sorption of aldol products together with the acetaldehyde itself by the resin. Absorption maxima of the aldol products shifts to longer wavelengths due to increasing conjugation in time. This conjugation is the cause of the observed high absorption around 480 nm for the residual acetaldehyde in the solution. As a result, the sorbed amounts found for the acetaldehyde are erroneously lower than for the other aldehydes.

Due to this fact, the amount sorbed is virtually lower than the expected values. The same argument is valid also for the sorption kinetics, that the kinetic curve of acetaldehyde lies under those of the other aldehydes.

In order to compare the aldolization behaviour of butyraldehyde, it was left in contact with the resin for 4 h in methanol solution. The shift in its absorption maxima (323 nm) was only 30 nm which is far below the 480-nm wavelength. Thus, aldol condensation for butyraldehyde proceeds slowly and caused practically no complications in 3 h of interactions in the loading experiments studied.

In comparison to benzaldehyde, salicylaldehyde binding is higher and faster than the former. Most probably the acidic character of the phenolic OH group in salicylaldehyde is responsible for its high uptake, due to the basicity of the resin itself. Aldehyde binding can easily be followed by the FT-IR spectra of the benzaldehyde-loaded polymer. Aromatic C–H stretching vibrations of the involved phenyl ring are clearly observed at 3050 and 3080 cm^{-1}. These vibrations are not observed for the original polymer because of its aliphatic structure. This evidence is a clear-cut distinction of the benzaldehyde incorporation into the structure (Fig. 3).

Sorptions of aldehydes obey second-order kinetics. Rate constants for all the aldehydes (except acetaldehyde) are in the 1.5×10^{-2} to 2×10^{-2} mol^{-1} s^{-1} range.

From the kinetic curves in Fig. 1, it is clearly seen that the sorption rates are in the order: butyraldehyde > salicylaldehyde > benzaldehyde > acetaldehyde. It is interesting to note

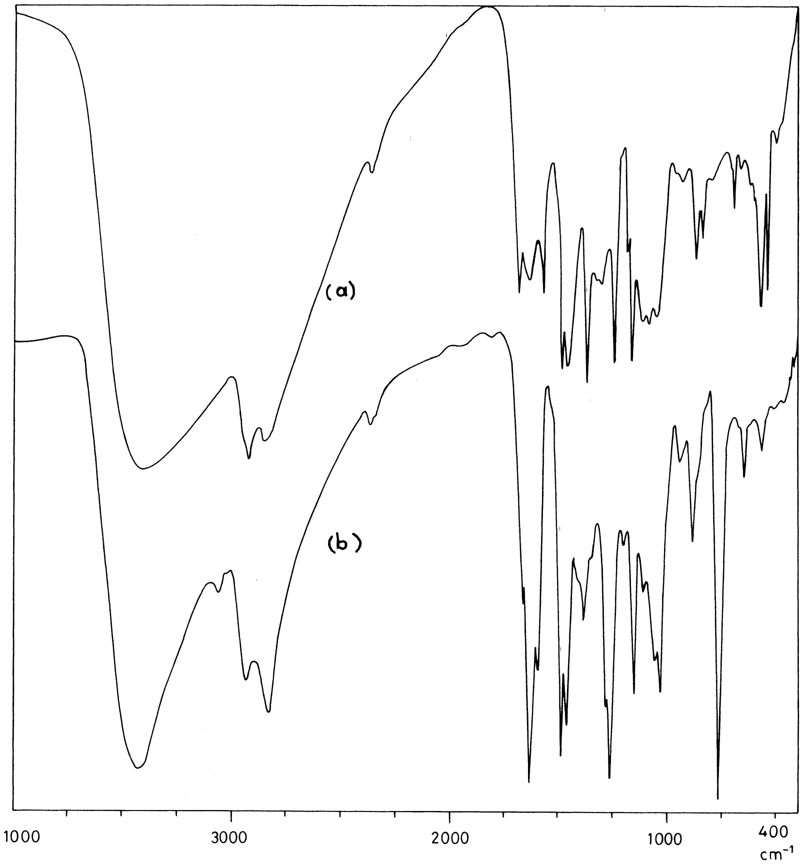


Fig. 3. FT-IR spectra of the resin (a), and the resin loaded with benzaldehyde (b).

that aldehyde sorption is drastically lower in cyclohexane than in methanol and dioxane solvents (Fig. 2). This seems to be in accordance with the polarity of the solvent used, because the resin itself is hydrophilic and is not compatible with hydrocarbon solvents, such as cyclohexane; whereas, in our previous paper, we have demonstrated that oligoethyleneimines attached to polystyrene sulphonamide resin are capable of aldehyde uptake from both hydrocarbon and polar solvents [13]. In that case hydrophilic–lipophilic balance of the polymer structure permits interaction with polar and nonpolar solvents. As a consequence, hydrophilic–lipophilic balance is an important factor governing aldehyde sorption, just as pointed out in previous metal-uptake experiments on some polymers [14]; whereas, in our case, the polymer is hydrophilic in nature and sorption occurs preferably in polar solvents.

3.2. Recovery of the sorbed aldehydes and regeneration of the resin polymer

Aldehydes were stripped from the loaded polymer samples by interacting with the methanol–HCl (2 M) solution (1:1). The amounts of stripped aldehydes were measured by monitoring aldehyde concentrations of the acid solutions. These experiments show that aldehyde desorptions do not complete in 3 h of interaction period and 43–67% of the sorbed amounts are eluted (Table 1).

The high swelling ability of the resin in the acid must be another factor affecting on the desorption, because diffusion of the released aldehydes forms the swollen polymer matrix into the solution must be inhibited. The swelling ratio of the polymer in 1 M HCl solution is about 16.0 (W/W_0), which can be considered to be responsible for the slow desorptions.

However, additional experiments indicate that, within 5 h of interaction with 5 M HCl solutions, all the sorbed aldehydes are released completely from the loaded polymer samples.

Additionally, to compare the desorption rates of aromatic and aliphatic aldehydes, desorptions of benzaldehyde and butyraldehyde were followed kinetically. Fig. 4 represents that the desorption of butyraldehyde is faster than that of benzaldehyde probably because of the higher hydrophilicity of the former. Relatively higher hydrophilicity facilitates the diffusion of acid solution into the loaded polymer and this results in fast desorption of butyraldehyde.

The last step is regeneration of the used polymer. After a complete desorption of the aldehydes, the amino groups are in HCl form. The polymer at this stage can readily be transformed into free-amine form, simply by contact with 1 M NaOH solution for 24 h. After washing with excess of water and drying, the polymer becomes regenerated and is essentially ready for use in the next cycle. Indeed comparison of the IR spectra of the original polymers with those of the regenerated one, reveals that the two samples have the same IR pattern.

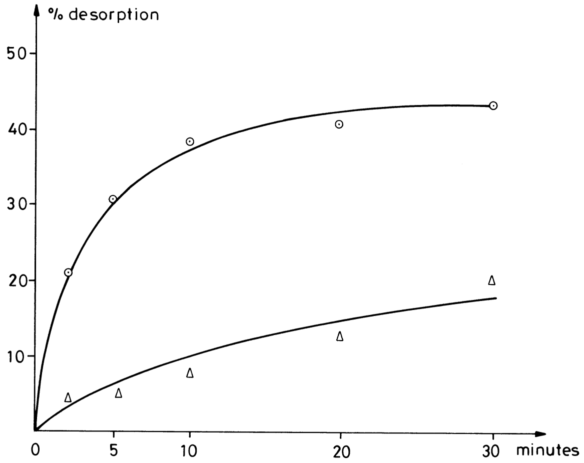


Fig. 4. Percentage aldehyde releasing from the resin in methanol/2 M HCl (1:1) solution. Butyraldehyde (⊙), benzaldehyde (△).

3.3. Interferences in the aldehyde sorption

Although we did not carry out quantitative competitive experiments, a qualitative test with acetone apparently indicates that acetone is bound to the polymer after contact for 5 days. Also, in acetic acid we did not observe any aldehyde sorption, due to inhibition of the nucleophilicity of the secondary amino groups. Alkyl halogenides also are considered to be efficient interfering agents due to their alkylating effects on the secondary amines.

In conclusion, 1,2-diamino ethane units in the epoxy–amine resin described can be used to extract aldehydes from relatively polar solvents or mixtures. Recovery of aromatic aldehydes is quite possible. Aliphatic aldehydes, except acetaldehyde, can also be recovered provided that interaction period is less than 3 h. In the case of long-term interactions with aliphatic aldehydes with α-hydrogen, aldol condensation (Claisen–Schmidt) products form during the sorption. This can be considered as the most important limitation of the polymer use for aliphatic aldehydes. However, if the recovery of aldehyde is not the aim, the polymer can be used for the removal of trace quantities of aliphatic aldehydes.

Moreover, not having hydrolysable groups, the polymer is quite stable towards acid and base hydrolyses. This is another important factor for recycling of the polymer, especially from the point of view of practical applications Furthermore, this analogy seems to be general for all 1,2-diamino ethanes and can be extended to the other polymers having 1,2-diamino ethane units in the main or side chains. Finally, the crosslinked polymer is accessible from commercially available chemicals, and the method presented is very promising for large-scale applications.

Acknowledgements

Financial support of the Istanbul Technical University Research Foundation is greatly acknowledged.

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