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Site–site interactions in a polymer matrix: effect of amine structure on transformations of copoly(styrene–*p*-nitrophenylacrylate)

Marko Zupan*, Peter Krajnc and Stojan Stavber
Laboratory for Organic and Bioorganic Chemistry, Department of Chemistry and 'J. Stefan' Institute, University of Ljubljana, Slovenia
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Crosslinked copoly(styrene–*p*-nitrophenylacrylate)s (**1a**, **1b** and **1c**, containing 2, 4 and 10% divinylbenzene, respectively) reacted readily with secondary amines (piperidine, morpholine, piperazine, *N*-phenylpiperazine), the course of substitution being influenced by the crosslinking of **1**, solvent polarity (dimethylformamide, methanol, toluene) and the structure of the amine. Steric interactions influenced the transformation of **1a** with various primary amines (n-butylamine, i-propylamine and cyclohexylamine) giving the corresponding amides; tertbutylamine and aniline do not transform **1a** under similar reaction conditions (dimethylformamide, $T = 50°C$). The swelling ability of the resins depended on the crosslinking of the starting copoly(styrene–*p*-nitrophenylacrylate) (**1**), the structure of the amide and solvent polarity (water, methanol, dimethylformamide, toluene, chloroform, cyclohexane). Copyright © 1996 Elsevier Science Ltd.

(Keywords: crosslinked copoly(styrene–*p*-nitrophenylacrylate); nucleophilic substitution; primary and secondary amines)

INTRODUCTION

Functionalization of polymer resins represents an interesting and important technique for the preparation of new reagents, catalysts, separation media, etc. Chemical reactions of polymer resins with reagents where difunctionalization is possible can result in additional crosslinking. The concomitant change in the polymer backbone structure can significantly influence the physical properties of the carrier, which are reflected in changed behaviour of the resulting catalysts, reagents or carriers for separation media[1–19]. The introduction of various basic units into a polymer matrix represents an interesting method for the preparation of new polymer carriers for various purposes. It is very important to use an appropriate substrate for immobilization of a reagent in an insoluble polymer matrix, because immobilization is usually reflected in much easier-to-handle reagents but reactivity is modified or completely changed, while the formation of too stable a product could result in complete unreactivity of the polymer-supported reagent or catalyst. However, there is only a very limited amount of information that can help us to predict the role of the insoluble matrix structure in immobilization.

Crosslinked polystyrene is the most studied carrier and various reports have appeared dealing with additional crosslinking during the introduction of different functional groups into the polymer backbone. One property of polystyrene-based resins that is changed most disadvantageously is the swelling behaviour. However, it has been demonstrated that the substitution of some styrene units by acrylic esters and amides has a great influence on the swelling behaviour, and Arshady and co-workers have made an important contribution to the use of this type of polymer[20–22]. The introduction of a carboxylic group into the polymer network can dramatically change the properties of the carrier, internal polarity and swelling capacity being the most important of these (hydrophobic–hydrophilic interactions). On the other hand, the carboxylic functional group offers many possibilities for the introduction of further (different) functional groups: basic units, for example, are very important for the preparation of catalysts, reagents, separation media, etc.[23,24].

In this paper, we report the results of further investigations concerning the effect of polymer backbone flexibility on additional crosslinking during the functionalization of a polymer resin[25–27].

EXPERIMENTAL

Materials

Commercially available piperidine (Fluka), morpholine (Aldrich), piperazine (Aldrich), *N*-phenylpiperazine (Aldrich), n-butylamine (Aldrich), cyclohexylamine (Kemika), isopropylamine (Fluka), t-butylamine (Fluka), *p*-nitrophenol (Fluka), *p*-tertbutylphenol (Aero), acryloylchloride (Fluka), triethylamine (Fluka), hydrochloric acid (Kemika), azobisisobutyronitrile (AIBN; Fluka), poly(vinylpyrrolidone) (Fluka) and sodium hydrogencarbonate (Kemika) were used as received. Divinylbenzene (DVB; a 50/50 mixture ethylstyrene and isomeric divinylbenzenes, Merck) was washed with NaOH (5%)

* To whom correspondence should be addressed

and water, and dried over anhydrous Na_2SO_4 before use. The degree of functionalization of resins was determined by Fourier transform infra-red (*FT*i.r.) spectroscopy (Perkin–Elmer FT-IR 1720X) and combustion analysis (Perkin–Elmer 2400 CHN). *p*-Nitrophenylacrylate and *p*-tertbutylphenylacrylate were prepared by literature methods[22,28].

*Preparation of crosslinked copoly(styrene–p-nitrophenylacrylate) (**1a**, **1b**, **1c**)*

A suspension polymerization reactor was charged with 10 g of poly(vinylpyrrolidone) dissolved in deionized water (1.5 dm^3) which was degassed under reduced pressure for 15 min. The solution was heated to 80°C and, under stirring, a chlorobenzene solution of monomers, crosslinker and radical initiator was added (30 cm^3 of chlorobenzene, 15.96 g of *p*-nitrophenylacrylate, 8.54 g of styrene, 1.02 g (**1a**) or 2.13 g (**1b**) or 6.12 g (**1c**) of dinvylbenzene, 1 g of AIBN). The reaction mixture was stirred for 3 h at 80°C, for 2 h at 90°C and then cooled. The polymer beads were filtered, washed with dimethylformamide (3 × 20 cm^3), and chloroform (3 × 20 cm^3), and dried at room temperature for 20 h. The following amounts of air-dry products were isolated: 25.59 g of **1a** (crosslinking DVB 2%), 21.45 g of **1b** (crosslinking DBV 4%) and 25.33 g of **1c** (crosslinking DVB 10%).

Polymer beads of size distribution between 0.1 and 1 mm were analysed by infra-red spectroscopy. For combustion analysis, 1 g of air-dry products were further dried for 3 h at 110°C *in vacuo* and dry samples were obtained with the following compositions.

- 0.75 g of **1a** (crosslinking DVB 2%): %C = 70.28, %H = 4.93, %N = 4.62; 3.3 meq *p*-nitrophenyl groups per g;
- 0.81 g of **1b** (crosslinking DVB 4%): %C = 71.06, %H = 5.12, %N = 4.51; 3.2 meq *p*-nitrophenyl groups per g;
- 0.96 g of **1c** (crosslinking DVB 10%): %C = 71.98, %H = 5.45, %N = 4.17; 3 meq *p*-nitrophenyl groups per g.

*Reactions of crosslinked copoly(styrene–p-nitrophenylacrylate) (**1a**, **1b**, **1c**) with amines*

Copoly(styrene–*p*-nitrophenylacrylate), 1.58 g of **1a**, (2% DVB) or 1.47 g of **1b** (4% DVB) or 1.71 g of **1c** (10% DVB), was suspended in 30 cm^3 of dimethylformamide (as well as in methanol and toluene in the case of **2a**, **5a** and **6a**) and the appropriate amount of amine was added (1.24 g of morpholine, 0.88 g of i-propylamine, 1.27 g of piperidine, 1.09 g of n-butylamine, 1.49 g of cyclohexylamine, 2.43 g of *N*-phenylpiperazine or 1.29 g of piperazine). The reaction mixture was heated at 50°C under stirring for 5 h (for 10 h in the case of **1c** in dimethylformamide). The solid product was filtered off, washed with dimethylformamide (3 × 10 cm^3) and methanol (3 × 10 cm^3), and dried at room temperature for 20 h. The following amounts of products were isolated:

- piperidino derivatives (**2**): 0.89 g (**2a**), 0.82 g (**2b**), 1.34 g (**2c**),
- morpholino derivatives (**3**): 1.04 g (**3a**), 0.95 g (**3b**),
- *N*-phenylpiperazino derivative (**4**): 1.26 g,
- piperazino derivatives (**5**): 0.94 g (**5a**), 1.04 g (**5b**),
- n-butylamino derivatives (**6**): 0.85 g (**6a**), 0.92 g (**6b**),
- isopropylamino derivatives (**7**): 0.76 g (**7a**), 0.72 g (**7b**),
- cyclohexylamine derivative (**8**): 1.16 g.

A quantity (100 mg) of air-dry polymer beads was further dried for 3 h *in vacuo* at 80°C or 110°C. The progress of substitution was monitored by i.r. spectroscopy, while completely substituted samples were analysed by combustion analysis.

Piperidino derivatives (**2**):
- **2a**: 87 mg; %C = 78.44, %H = 9.46, %N = 5.59 (4.0 meq piperid. groups per g); 110°C;
- **2b**: 91 mg; %C = 78.64, %H = 8.98, %N = 5.67 (4.1 meq piperid. groups per g); 80°C;
- **2c**: 96 mg; %C = 79.41, %H = 8.61, %N = 5.05 (3.6 meq piperid. groups per g); 80°C.

Morpholino derivatives (**3**):
- **3a**: 90 mg; %C = 73.79, %H = 8.23, %N = 5.57 (4.0 meq morph. groups per g); 110°C;
- **3b**: 96 mg; %C = 73.79, %H = 8.10, %N = 5.91 (4.2 meq morph. groups per g); 80°C.

N-Phenylpiperazino derivative (**4**):
- 85 mg; %C = 76.86, %H = 7.60, %N = 8.71 (3.1 meq *N*-phenylpip. groups per g); 80°C.

Piperazino derivatives (**5**):
- **5a**: 81 mg; %C = 72.55, %H = 8.68, %N = 9.60 (3.4 meq piperaz. groups per g); 110°C;
- **5b**: 88 mg; %C = 72.98, %H = 8.27, %N = 9.89 (3.5 meq piperaz. groups per g); 80°C.

n-Butylamino derivatives (**6**):
- **6a**: 83 mg; %C = 77.02, %H = 9.90, %N = 5.72 (4.1 meq n-butylamino groups per g); 110°C;
- **6b**: 90 mg; %C = 77.34, %H = 9.34, %N = 5.98 (4.3 meq n-butylamino groups per g); 80°C.

Isopropylamino derivatives (**7**):
- **7a**: 89 mg; %C = 77.22, %H = 9.13, %N = 6.37 (4.6 meq i-propylamino groups per g); 80°C;
- **7b**: 91 mg; %C = 76.41, %H = 8.66, %N = 6.00 (4.3 meq i-propylamino groups per g); 80°C.

Cyclohexylamine derivative (**8**):
- 82 mg; %C = 78.91, %H = 9.78, %N = 5.28 (3.8 meq cyclohexylamino groups per g); 110°C.

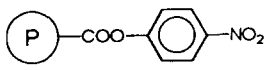
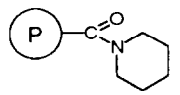
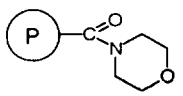
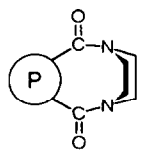
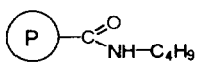
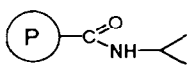
Determination of resin swelling capacity

A small volume (1 cm^3) of air-dry polymer resin was weighed and placed in a graduated cylinder. Solvent (10 cm^3) was then added and the volume of swollen beads was measured after 24 h. The swelling capacities per g are presented in *Table 1*.

RESULTS AND DISCUSSION

Arshady and co-worker prepared various crosslinked styrene–acrylate copolymers, usually using 2,4,5-trichlorophenylacrylate as monomer (chloro-substituted phenol is not commercially available)[20–22]. In order to find some more accessible and convenient acrylate ester, we first studied the polymerization of the styrene–*p*-nitrophenylacrylate system and found that the use of a 1 : 1 reaction mixture in chlorobenzene as solvent in the presence of AIBN at 70°C gave a polymer where the ratio between the styrene and acrylate units remained the same as in the reaction mixture (the ratio was determined by elemental

Table 1 Effect of crosslinking and polymer structure on swelling in various solvents[a]

Structure	Polymer	DVB content (%)	$cm^3 g^{-1}$ [b]	Solvent				
				CH_3OH	DMF	$CHCl_3$	$PhCH_3$	C_6H_{12}
	**1a**	2	1.9	1.9	7.5	7.9	3.8	2.3
	1b	4	1.7	1.7	5.9	5.9	3.1	2.0
	1c	10	1.3	1.3	3.3	3.3	2.8	1.6
	**2a**	2	2.5	5.0	7.0	15.0	6.3	4.5
	2b	4	2.4	3.9	4.6	7.3	6.3	4.5
	2c	10	1.8	2.1	2.8	4.4	4.2	2.1
	**3a**	2	2.3	3.3	10.2	13.7	5.8	4.0
	3b	4	2.1	3.1	5.0	7.1	5.2	2.5
	**5a**	2	2.2	5.3	5.8	8.9	2.4	2.9
	5b	4	2.1	5.0	3.8	5.2	2.3	2.7
	5c	10	2.0	3.3	2.7	4.1	2.3	2.2
	**6a**	2	2.2	2.6	3.9	14.8	5.2	2.6
	6b	4	2.0	2.4	3.6	8.4	5.2	2.2
	**7a**	2	2.2	9.1	11.9	13.0	5.5	3.1
	7b	4	2.1	4.8	6.5	7.9	5.5	2.7

[a] Swelling capacity in cm^3 of swollen beads per g of air-dry resin
[b] Volume of 1 g of air-dry resin

analysis and ^1H nuclear magnetic resonance spectroscopy). Suspension polymerization in the presence of 2, 4 or 10% of divinylbenzene gave polymer beads containing the following amounts of acrylate equivalents per g (established by elemental analysis): 3.3 meq g^{-1} for **1a** (2% DVB), 3.2 meq g^{-1} for **1b** (4% DVB) and 3 meq g^{-1} for **1c** (10% DVB).

The addition–substitution reactions of carboxyl functional groups are usually strongly influenced by steric effects and the structure of the leaving group. For this reasons, we studied the effect of the leaving group (*p*-nitrophenoxy *versus p*-tertbutylphenoxy) and degree of crosslinking on reactions with piperidine in dimethylformamide. Transformations were followed by *FT*i.r. spectroscopy and as, evident from *Figure 1*, the signal for the ester group at $\nu = 1755\,cm^{-1}$ disappeared and the amide signal at $\nu = 1640\,cm^{-1}$ appeared. Good control of the degree of substitution of the leaving group could be obtained in the case of *p*-nitrophenol, as judged by the disappearance of the signal at $\nu = 1345\,cm^{-1}$. Complete substitution was achieved with 2% crosslinked beads in dimethylformamide at 50°C after 5 h; similar reactivity was also observed with 4% crosslinked resin, while 10 h were required for complete conversion of the 10% crosslinked resin (**1c**) to piperidino derivative **2c** in dimethylformamide. On the basis of elemental analysis, the following amounts of piperidino groups were determined: 4.0 meq g^{-1} for **2a**, 4.1 meq g^{-1} for **2b** and 3.6 meq g^{-1} for **2c**. Under the above-mentioned conditions the tertbutylphenoxy derivative remained almost unchanged, and for this reason in further investigations we used only *p*-nitrophenoxy derivatives (**1a**, **1b**, **1c**). Reactions proceeding via rehybridization of carbon atoms are usually highly dependent on the solvent, but in the case of insoluble resins their swelling capacity also becomes very important. Good swelling of supports enables better contact between the reagent and the functional group in the polymer matrix, and this becomes even more important when functional groups are attached close to the polymer backbone (no use of spacer). The 2% crosslinked resin was transformed with piperidine in dimethylformamide completely after 5 h at 50°C, while in toluene a lower degree of substitution was achieved. Substitution reactions also proceeded very well with morpholine and *N*-phenylpiperazine, thus forming resins **3a** (4.0 meq morpholino groups per g), **3b** (4.2 meq morpholino groups per g), and **4** (3.6 meq *N*-phenylpiperazino groups per g) (*Scheme 1*).

We further studied the possibility of additional crosslinking in crosslinked copoly(styrene–*p*-nitrophenylacrylate) (**1**) in its reactions with piperazine. Substitution of the *p*-nitrophenoxy group in **1a** occurred after 5 h at 50°C in dimethylformamide, beads containing 3.4 meq piperazino groups per g of resin were obtained (**5a**) (monofunctionalization of **1a** would give 4 meq piperazino groups per g, while complete disubstitution would deliver a resin containing 2.4 meq per g). In the functionalization of crosslinked chloromethylated polystyrene with piperazine under similar reaction conditions additional crosslinking was also established[25]. The reaction of 4% crosslinked resin (**1b**) with piperazine gave **5b**, containing 3.5 meq piperazino groups per g (monofunctionalization of **1b** would give 4 meq piperazino groups per g and complete disubstitution 2.4 meq per g). It is known that additional crosslinking can be influenced by the reaction temperature, and for this reason we conducted

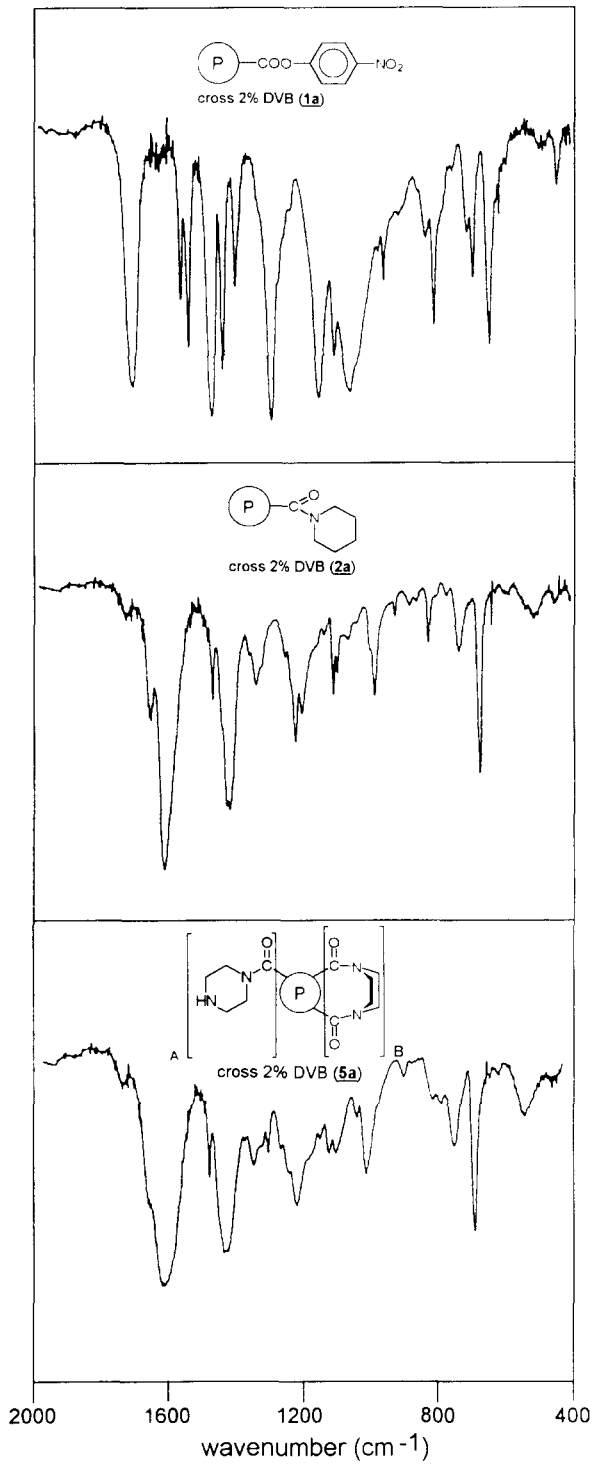
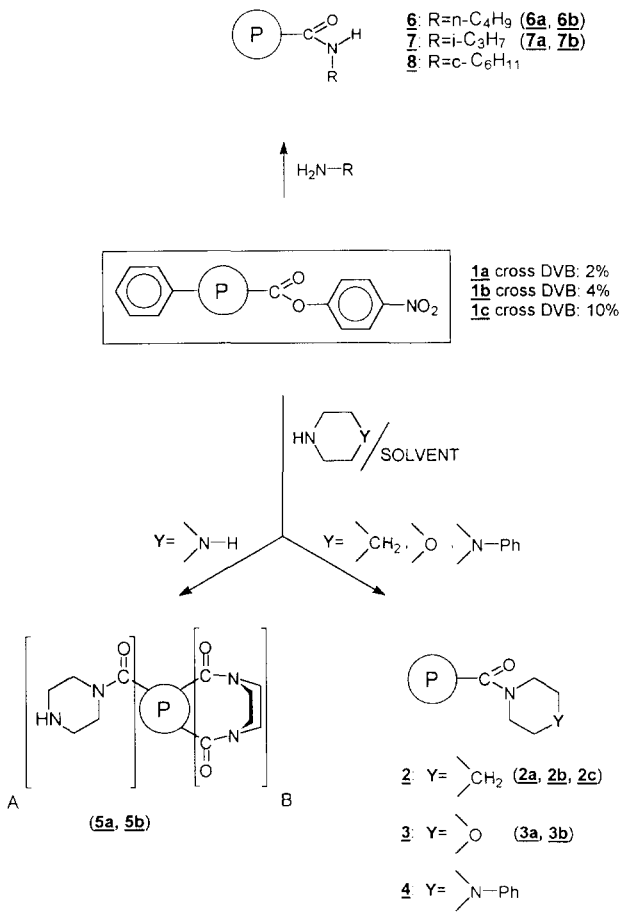


Figure 1 *FT*i.r. spectra of various resins

reactions with **1a** and **1b** in dimethylformamide with piperazine at room temperature for 24 h, no change in the course of the transformation was found. Solvent polarity also has an important role in functionalization of **1a** with piperazine. Complete conversion was found in dimethylformamide, the process in toluene required a longer reaction time, while transformations in chloroform and methanol were almost negligible after 5 h at 50°C. In *Figure 1* the *FT*i.r. spectra of various resins are presented.

We also investigated reactions of crosslinked copoly(styrene–*p*-nitrophenylacrylate) (**1**) with various primary



Scheme 1

amines. The *para*-nitrophenoxy group was completely replaced by n-butylamine in dimethylformamide at 50°C in 5 h and resin **6a** containing 4.1 meq n-butylamino groups per g (monofunctionalization of **1a** would give 4.1 meq n-butylamino groups per g, while complete disubstitution would give 2.5 meq per g) was isolated. Similar substitution also occurred with i-propylamine and resin **7a** containing 4.6 meq i-propylamino groups per g was isolated (monofunctionalization of **1a** would give 4.5 meq i-propylamino groups per g, while complete disubstitution would result in 2.6 meq per g). Monofunctionalization was also observed in the reaction with cyclohexylamine, giving the resin containing 3.8 meq cyclohexylamine groups per g (**7a**) (calculated for monofunctionalization: 3.8 meq of cyclohexylamine groups). Under the above-mentioned conditions, no transformation of **1a** with tertbutylamine or aniline was observed.

Finally, we studied the effect of crosslinking of copoly(styrene–*p*-nitrophenylacrylate) (**1**) and solvent polarity on reactions with n-butylamine. Substitution occurred almost completely with **1a** in toluene but only partly in methanol. A higher degree of crosslinking of the resin **1** was reflected in the longer reaction times needed for complete substitution with n-butylamine in dimethylformamide at 50°C, and the functionalization observed was 4.3 meq n-butylamine groups per g of **6b** (monofunctionalization of **1b** would give 4.1 meq n-butylamino groups per g, complete disubstitution would give 2.5 meq per g). The effect of crosslinking and polymer structure on swelling in various solvents is presented in *Table 1*. It

is evident that chloroform swells functionalized polymers much more than resins containing the *p*-nitrophenoxy group, while the DVB content plays a very important role and diminishes swelling. From the table the important role of the substituent on swelling in methanol is also evident: the isopropylamine derivative (**7a**) swells almost twice as much as the piperidino derivative (**2a**), while very poor swelling in methanol and dimethylformamide was found with the n-butylamino derivative (**6a**).

The present study again demonstrates how very difficult it is to predict flexibility in polymer beads. However, the novel carriers prepared here represent good examples for further studies on the effect of polymer backbone structure on the role of reagent and catalyst immobilization in polymer matrices.

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