Macromolecules **1981**, *14*, 1515–1518

Cross-Linker Effectiveness in Styrene Copolymerization

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ABSTRACT: Toluene swellings of copolymers of styrene with a number of multifunctional acrylate and methacrylate esters are reported as a function of cross-linker content. Comparisons are made with published figures for divinylbenzene and diisopropenylbenzene copolymers and hitherto unreported figures for divinyl sulfone– and divinyl ketone–styrene copolymers. The most appropriate figure to describe the cross-linking is shown to be the molar percent of "excess" vinyl groups in the monomer mixture. Cross-linking monomers with functionality as high as $f = 8$ have been investigated, and the various controlling factors are discussed.

Introduction

Without the property of insolubility, an ion-exchange resin would have a very short lifetime. Although polymers need not be chemically cross-linked to show insolubility, the conventional polystyrene-based ion exchangers are almost without exception derived from copolymers of styrene with a cross-linking agent. One of the least expensive and most commonly used is divinylbenzene; commercial DVB is essentially a mixture of meta and para isomers of divinyl- and ethylvinylbenzenes, with a divinylbenzene isomer content between 50 and 60%, except for special purposes.

It has been established that the toluene weight swelling,[1] or toluene regain,[2] of a DVB-cross-linked polystyrene gel is a measure of the matrix cross-linking. However, practical cross-linked polystyrene matrices are all sufficiently highly cross-linked that there is essentially no sol fraction, and the average intra-cross-link chain length is by conventional standards very low. In consequence, the assumption of simple network theory[3] that the chain between cross-links may be treated as a statistical chain is no longer valid, and direct calculation of cross-link density from equilibrium swelling is not feasible. In addition, there is appreciable contribution to the restraint on swelling from true trapped entanglements, the extent of which is a rapidly increasing function of the covalently-bonded cross-linker content.[4] Although it seems that for systems with minor amounts of cross-linking such entanglements play no part in determining their elastic properties,[5] this is clearly not so for the equilibrium swelling of networks of the type considered here. It is thus convenient to describe the extent of cross-linking in such matrices, particularly when further cross-linking of a different kind occurs or a different cross-linking agent is used, in terms of the "effective cross-linking" expressed as equivalent percent of DVB.

It should be noted that comparisons of effectiveness of cross-linking can be made on a number of bases. Clearly, the simplistic comparison by weight/weight percent of cross-linker is of limited validity. It enables cost effectiveness to be calculated, but little else. The present work has been limited to copolymerizations with styrene, but the range of cross-linkers considered makes it necessary to use a molar percent basis for comparison.

Either to avoid the restrictions of certain master patents or for the sake of special properties in the product, a number of other, and purer, cross-linking agents have been used, though few details of their effectiveness in cross-linking have been published. In many early ion-exchange patents[6,7] the cross-linker was disclosed merely as a polyvinyl aromatic compound, examples including such exotics as divinylnaphthalene or trivinylbenzene. Later patents disclosed polyvinyl compounds which were *not* aromatic, such as ethylene glycol dimethacrylate (EDMA)[8] or divinyl ketone (DVK),[9] as well as others, such as divinyl oxalate or vinyl methacrylate. More recently, special properties have been claimed for acrylic ester derivatives of polyols, such as trimethylolpropane trimethacrylate (TMPTMA), neopentyl glycol dimethacrylate (NPGDMA), or pentaerythritol tetramethacrylate (PETMA).[10] Some materials of higher functionality are used in surface-coating technology, usually in the form of UV-curable polymers.[11] One such is the pentaacrylate ester of dipentaerythritol (DPEHPA), which as "SR-399" is commercially available from Sartomer Co.

The behavior of all these different types of cross-linking monomers, in terms of the constraint imposed on swelling of the matrix, is governed by a number of factors. It is the purpose of the present investigation to explore and, if possible, codify these.

Experimental Section

Monomers used were all commercial polymerization grades, with the exception of *p*-DVB, DVK, and divinyl sulfone (DVS), which were laboratory preparations,[12,13] redistilled before use. In two cases with cross-linkers of high functionality the purity of the cross-linker was such that a notional molecular weight and fractional average functionality had to be used. A sufficiently accurate determination was possible by proton magnetic resonance measurements in $CDCl_3$ solution, and these figures, rather than the midpoint of the range quoted by the manufacturers, have been used throughout. In SR-399, for example, the ratio of the acryloyl vinyl proton resonance (ca. 6.2 ppm) to the dipentaerythrityl methylene proton resonance (ca. 4.3 ppm) gave an average acryloyl substitution of 4.45 and, hence, a fractional average functionality of 8.9 for the sample used. In each series of experiments standard suspension polymerization techniques[14] were used with either (usually) azobis(isobutyronitrile) or benzoyl peroxide catalysts, the former at 0.2% and the latter at 0.5% by weight based on the monomers. Polymerization temperature was routinely 75–80 °C, with no special precautions to avoid the presence of oxygen, and polymerization was "finished" overnight at 82–90 °C. The beads were filtered, washed, and dried in a vacuum oven at 85 °C. No absorption due to pendent double bonds was observed in the infrared absorption spectra, except at very high cross-linker contents, e.g., over 20% DVB.[4c] Recorded yields were in every case well over 90% by weight of the added monomers, with handling loss probably accounting for up to a further 5%. Toluene regains were measured, as previously described,[1,4] by means of a centrifugation technique. Details of cross-linkers used are summarized in Table I.

Results and Discussion

Since much of this work is concerned with acrylic ester cross-linkers of various sorts, it should first be pointed out that the intrinsic swellability in toluene of their copolymers with styrene is affected only to a negligible extent by a change in chemical composition. Table II gives solubility parameters[15] relevant to the monomeric and (where available) the linear polymeric model compounds. For a poorly hydrogen-bonded solvent like toluene, the difference

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Table I
Cross-Linking Properties

cross-linker	code	source	% purity	mol wt	functionality
divinylbenzene solution	DVB	Dow Chemical	~55[a]	130	4
p-divinylbenzene	*p*-DVB	*b*	>95	130	4
diisopropenylbenzene	DIPB	*c*	>95	158	4
divinyl ketone	DVK	*d*	>95	82	4
divinyl sulfone	DVS	*e*	>95	118	4
ethylene glycol dimethacrylate	EDMA	Anchor Chemical, J. T. Baker	>95	198	4
1,3-butylene glycol dimethacrylate	BGDMA	Sartomer	>95	226	4
1,3-butylene glycol diacrylate	BGDA	Sartomer	>95	198	4
triethylene glycol dimethacrylate	TEGDMA	Sartomer	>95	286	4
neopentyl glycol dimethacrylate	NPGDMA	Sartomer	>95	240	4
1,6-hexanediol dimethacrylate	HDDMA	Sartomer	>95	254	4
1,6-hexanediol diacrylate	HDDA	Celanese	>95	226	4
trimethylolpropane trimethacrylate	TMPTMA	Sartomer	>92	338	6
trimethylolpropane triacrylate	TMPTA	Celanese	>95	296	6
pentaerythritol tetramethacrylate	PETMA	Monomer-Polymer	>95 tetra	408	8
pentaerythritol tetraacrylate	PETA	Sartomer	54 tetra	307[f]	6.4[f]
dipentaerythritol monohydroxy pentaacrylate	DPEHPA	Sartomer	45 penta, 55 tetra	495[f]	8.9[f]

[a] 45% ethylstyrene and 37% *m*- and 18% *p*-divinylbenzenes. [b] Laboratory preparation,[12] mp 29-30 °C. [c] 68% *m*- and 31% *p*-diisopropenyl benzenes.[16] [d] Laboratory preparation,[13] bp 35 °C (20 mm). [e] Laboratory preparation,[13] bp 101-103 °C (10 mm). [f] From ^{1}H NMR determinations in $CDCl_3$, using tetramethylsilane as internal standard.

Table II
Solubility Parameters (cal cm^{-3})$^{1/2}$ for Carboxylate Esters Ketones, Sulfones, and Aromatics[a]

methyl propionate	8.9	benzene	9.15
ethyl acetate	9.1	toluene	8.91
ethyl propionate	8.4	*p*-cymene	8.2
n-butyl propionate	8.8	ethylbenzene	8.8
	av ~8.7		av ~8.8
poly(ethyl acrylate)	9.4	polystyrene	9.1
poly(*n*-butyl acrylate)	8.8	poly(styrene-*co*-divinylbenzene)	9.1
poly(methyl methacrylate)	9.2	poly(vinyltoluene)	8.9
			av ~9.0
poly(*n*-propyl methacrylate)	8.8		
poly(*n*-hexyl methacrylate)	8.6		
	av ~9.0		
methyl ethyl ketone	9.3	diethyl sulfone	12.5
diethyl ketone	8.8	dipropyl sulfone	11.3
methyl *n*-propyl ketone	8.7		av ~11.9
	av ~8.9		

[a] Figures are quoted from ref 15b.

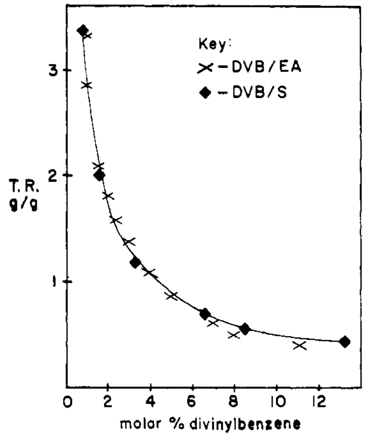


Figure 1. Comparison of toluene regains for DVB/EA and DVB/S copolymers as a function of DVB content.

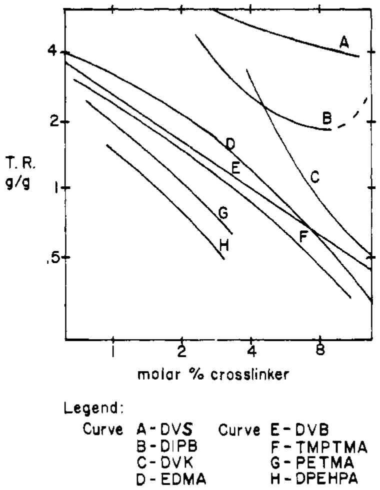


Figure 2. Toluene regain as a function of molar percent cross-linker for cross-linked styrene copolymers made with different cross-linkers. DIPB results are calculated from figures given in ref 16. They should be treated with caution for reasons given in the text.

in solubility parameter for the acrylic and the aromatic moiety is insignificant. Additional evidence for this is shown in Figure 1, where the observed toluene regains for DVB-cross-linked ethyl acrylate and styrene copolymers are compared.[12] Swellings, despite the difference in aromatic content, are quite similar over a tenfold range of cross-linker content.

Three main considerations affect the performance of a cross-linking agent: its functionality, its structure, and its state of dispersion throughout the network. Other things being equal, an increase in functionality of the cross-linking agent might be expected to increase its effectiveness. From simple network theory the critical value α_c of the branching probability, which relates to the *onset* of gelation, is crucially dependent on the average functionality f of the branching unit.[3] Certainly the gel stage in polymerization with $f > 4$ was observed to be appreciably earlier than with conventional 4-functional cross-linkers. Furthermore, this increased effectiveness is apparent in plots of regain vs. molar percent cross-linker (Figure 2). However, the same results, plotted in terms of the molar percent of excess vinyl groups (used in this context to include isopropenyl, acryloyl, and methacryloyl unsaturation) over and above

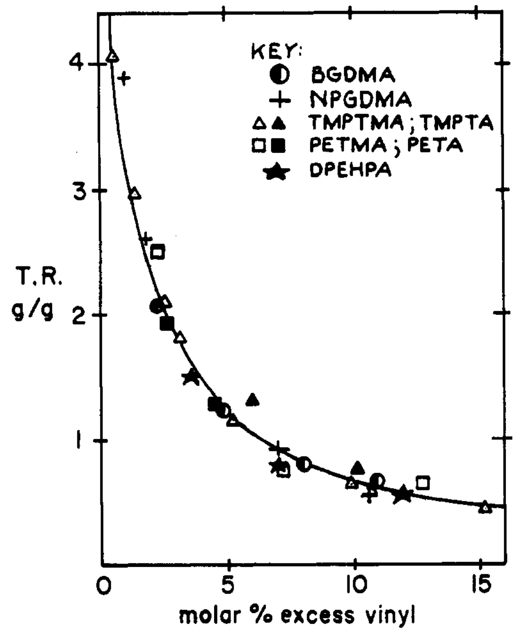


Figure 3. Toluene regain as a function of molar percent excess vinyl groups for cross-linked styrene copolymers made with branched cross-linkers.

Table III
Reactivity Ratios for Styrene (M_1) with Some Polyvinyl Compounds and Their Models

compound	r_1	r_2	T, °C	ref
	Aromatic			
m-DVB	0.61	0.88	80	20
p-DVB	0.77	2.08	80	20
m-DIPB	1.2	0.8	100	21
p-DIPB	0.61	0.00	100	21
1,2,4-TVB	1.80	1.12	70	22
α-MS[a]	1.3	0.3	60	23
	Aliphatic			
DVS	1.30	0.01	60	24
cf. MVS[a]	1.40	0.01	60	25
DVK	N/A	N/A		
cf. MVK[a]	0.29	0.35	60	26
EDMA	0.35	0.65	60	27
cf. MMA[a]	0.54	0.50	60	28
EMA[a]	0.65	0.29	70	29
MA[a]	0.75	0.20	70	30
EA[a]	0.80	0.20	70	29

[a] Model monovinyl compounds; M = methyl, E = ethyl, and A = acrylate.

that required for incorporation into the linear polymer, show no such increase (Figure 3). It should be noted that these results are all for cross-linkers of obviously branched structure, whose vinyl groups are essentially independent. The swellings shown, at any given cross-linking, are somewhat higher than for the comparable DVB copolymers[2] or those made with essentially unbranched acrylic cross-linkers, e.g., ethylene glycol dimethacrylate (Figure 4). The side-chain methyl groups of the methacrylate moiety in this context are not regarded as branching.

Also clear from Figure 3 and 4 is that, while in the acrylic/methacrylic esters the presence of an α-methyl group has little effect on cross-linking efficiency, this is not the case with the aromatic cross-linkers. Relevant reactivity ratios are given in Table III, from which it can be seen that m-DIPB is much less susceptible to attack by a styrene radical than m-DVB and, hence, has a very much lower tendency to "bunch" along the growing chain.

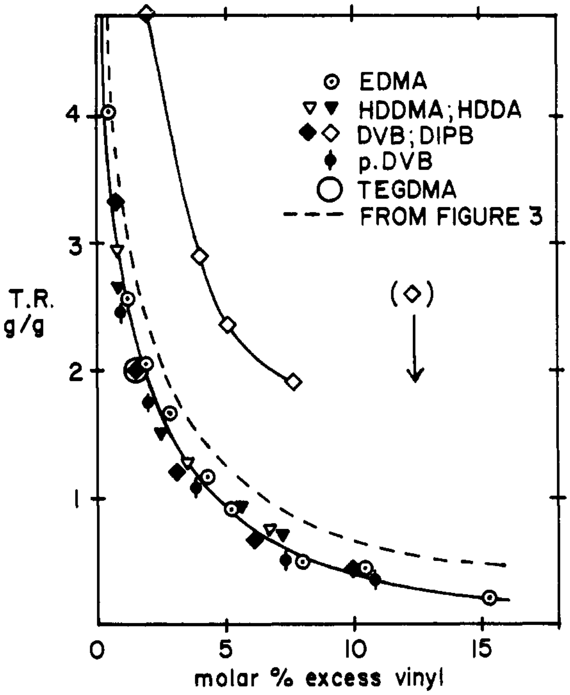
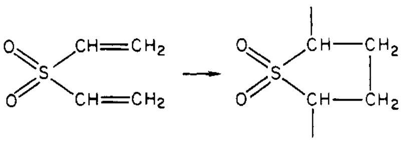


Figure 4. Toluene regain as a function of molar percent excess vinyl groups for cross-linked styrene copolymers made with unbranched cross-linkers. DIPB results are calculated from figures given in ref 16. They should be treated with caution for reasons given in the text.

With p-DIPB, the reactivity ratio r_1 (where M_1 is styrene) is very similar to that of m-DVB, and the incorporation of p-DIPB would be expected to parallel that of DVB. However, the pendent vinyl group no longer behaves like that of, for example, ethylstyrene but like α-methylstyrene (α-MS), with much lower (r_2) reactivity. There is also a possibility of chain transfer, which complicates the picture, but the overall effect is a marked decrease in cross-linking efficiency. The results quoted in Figure 4 for DIPB are taken from the work of Kolesnikov et al.,[16] who used a mixture of 68% m-DIPB and 31% p-DIPB and measured the benzene swelling of their copolymers. Benzene and toluene show closely similar volume swellings, and hence the corresponding toluene regain values could be calculated. Our own preliminary work with a sample of DIPB from CDF Chemie (France) indicates that all the swelling values from Kolesnikov's paper are too high, probably as a result of incomplete polymerization, which results in an expanded-structure network.[17] The isomer ratio of the French DIPB was essentially that of the Russian, with 65% m-DVB and 32% p-DIPB, the remainder being saturated aromatics. Our polymerization yields at 4 and 8 molar % DIPB were >98% of theory, with toluene regains, after extraction with dichloromethane to remove residual solubles, of 1.5 and 0.9 g/g, respectively, compared to 2.8 and 1.9 g/g (calculated) from the results in ref 16. These resins showed only minimal residual unsaturation.

Similar considerations apply to DVS, except that incorporation is not as rapid as for DVB, and the probability of intramolecular cyclization, which does not exist with m-DVB or p-DIPB, is relatively high.



Such cyclization, which gives a five-membered ring di-

Table IV
Effect of Intervinyl Distance in Cross-Linker

cross-linker	no. of bonds between vinyls		approx. distance	% cross-linker for TR = 2	
	C–C	C–O	d, Å	w/w	molar
EDMA	3	4	10	3.5	1.7
HDDMA	7	4	15	4.1	1.6
TEGDMA	5	8	18	4.6	1.6
DVB	(4)		6	2.0	1.6

functionally connected to the polymer chain, converts a potential tetrafunctional unit to an effectively difunctional unit and is analogous to the cyclopolymerization of *o*-divinylbenzene observed by Wiley and Davis.[18] As a consequence, DVS is by far the least efficient cross-linker for styrene copolymerization of those studied.

A corresponding intramolecular cyclization (also yielding a five-membered ring) occurs with DVK and results in some wastage of cross-linker at low DVK levels. However, judging by the reactivity ratios of model compounds, DVK is readily incorporated into the DVK–S copolymer chain with comparatively little chain transfer. The copolymers with higher DVK contents have swellings not too different from those of conventionally cross-linked copolymers.

Cyclization of the "extramolecular" type (i.e., cyclization due to the reaction of a pendent double bond with the growing end of its own main chain) occurs to varying extents in all vinyl–polyvinyl polymerizations. It has been estimated that between one-third and one-half of the cross-links in DVB/S or EDMA/S polymerizations are elastically ineffective for this reason.[19] There seems to be no indication from the results presented here that the cross-linkers of higher functionality are more prone to this (see Figure 3). The minor differences between branched and linear cross-linkers, however, may reflect more ready extramolecular cyclization in the former series.

Finally, we conclude from Figure 4 that the "flexibility", or chain length between the two vinyls of a tetrafunctional cross-linker, often believed to influence the effectiveness of cross-linking, apparently does not. A comparison of EDMA, HDDA, triethylene glycol dimethacrylate (TEGDMA), and DVB at a toluene regain of 2.0 g/g indicates little variation in the molar percent of cross-linker which is required (see Table IV).

Acknowledgment. Simon Martin, Evon Teng, and Ralph Snodgrass were responsible for most of the syntheses of the polyfunctional acrylate and methacrylate copolymers, and Chris Dyball gave us the benefit of his knowledge of polymerization in many helpful discussions. Our thanks are due to each one.

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