New Crosslinking Agents for Vinyl Polymers

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Synopsis

The synthesis of diallyl esters of linear dicarboxylic acids, and their use as multifunctional crosslinking agents for vinyl polymers, was studied. The number of carbon atoms in the chains of the diacids used varied from 2 to 10 in order to define the effect of the chemical structure on the reactivity of the crosslinkers prepared. Measurements of swelling in chloroform were performed to determine the average molecular weight between crosslinks, thus making an overall evaluation of the crosslinking efficiency. Sorption experiments were also carried out, using aqueous ethanol.

INTRODUCTION

The crosslinking of styrene with divinyl benzene during copolymerization allows its use in the manufacture of ion exchange resins as well as in gel permeation chromatography.[1] Furthermore, the copolymerization of methyl methacrylate with ethylene glycol dimethacrylate modifies poly(methyl methacrylate) to a polymer network with applications as biomaterial.[2,3]

Many studies investigate the copolymerization reaction of vinyl–divinyl compounds, in order to define the efficiency of crosslinking.[1,4-7] The above studies concluded that concentration and structure of the crosslinking agent have an influence on the efficiency of crosslinking, because of the resulting geometrical restrictions on the motion of unsaturated vinyl groups. The higher reactivities correspond to structures containing a long flexible chain between end groups, so that dimethacrylate esters of aliphatic diols or oligomers of ethylene glycol are commonly used. This class of crosslinkers presents the advantage of easy availability of various chain lengths of glycols and, therefore, offers the possibility to select the recommended compound for each case.

Although a simple process, the preparation of dimethacrylate esters, by esterification of methacrylic acid, includes some difficulties arising from the reactivity of methacrylic acid.[8] The use of inhibitors (such as hydroquinone) is therefore necessary during the esterification, because of the thermal stresses on the reaction mixture and product. In addition, the presence of residual inhibitor in the product can cause problems during the subsequent polymerization process, so a purification is also necessary.

To overcome these problems, and yet retain the versatility of dimethacrylates, synthesis and application of diallyl esters was carried out in this work. The use of aliphatic chain diacids in combination with the considerably less reactive (in respect to methacrylic acid) diallyl alcohol, seems to provide an alternative route for conventionally used crosslinkers for vinyl polymers. In

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fact, the aliphatic diacid series offers the possibility to select the desired chain length. Although allyl alcohol, as well as other allyl compounds, can be polymerized only with difficulty by free radical catalysts,[9] diallyl compounds react to form crosslinked structures even at relatively low conversions.[10]

The introduction of such new crosslinking agents, to be used for vinyl polymers instead of the extensively applied dimethacrylates, needs, of course, further investigation concerning the crosslinking reaction and the properties of crosslinked product. Literature data on the crosslinking efficiency and properties introduced by crosslinking, are compared with the behavior of diallyl crosslinkers.

For the crosslinking efficiency, a method has been proposed,[5] using the residual unsaturation which derives from the observed volume contraction with polymerization. Other methods provide intrinsic viscosity measurements[11] or the determination of the gel point.[12] The method of solvent swelling, which is extensively used in determining the average molecular weight between crosslinks, thus estimating the crosslinking density, seems to be a quick and effective way for an overall evaluation of the crosslinking efficiency.

When a specimen of crosslinked polymer is immersed in a suitable solvent, swelling occurs for the same reason that the solvent mixes spontaneously with an analogous linear polymer to form a polymer solution.[13] The swelling solvent must be therefore a good solvent for the linear analogues of the polymer network. When swelling equilibrium is reached, one can calculate the average molecular weight between crosslinks (M_c) through the following formula:

$$- \left[\ln(1 - v_2) + v + x_1 v_2^2 \right] = (v_1/\bar{v}M_c)(v_2^{1/3} - v_2/2) \qquad (1)$$

where $v_2 = v_0/v$, polymer volume fraction in the swollen network, $v_0 =$ polymer volume before swelling, $v =$ volume of swollen polymer in equilibrium state, $x_1 =$ interaction parameter for the polymer–solvent system, $v_1 =$ molar volume of the solvent, and $\bar{v} =$ specific volume of the polymer.

The term $(1 - 2M_c/M)$, commonly present as a correction factor for network imperfections due to chain ends, can be neglected under the assumption that the main molecular weight (M) equals infinity, i.e., the network is a perfect one.

Thus calculated, M_c can give an idea about crosslinks density, and, furthermore, taking into account the amount of crosslinker added, an overall picture of the crosslinking efficiency can be obtained. However, the M_c value alone does not predict the behavior of the crosslinked material. Thus, for a complete evaluation of the new crosslinker, some tests must be carried out in order to compare property changes in both cases.

Many properties were investigated, and their modification with crosslinking has been discussed. Thus, the changes of tensile strength,[14-17] tensile creep,[15,18-20] impact strength,[21,22] surface hardness,[15,16,18,19] and water sorption[14,23] for methyl methacrylate crosslinked with various dimethacrylate esters of glycols are discussed. In our work, sorption measurements were performed as a first characterization of the crosslinked materials prepared. Since the water sorption seems to remain unaffected by crosslinking, a more drastic mixture (50% aqueous ethanol) was selected.

EXPERIMENTAL

Materials

The allyl alcohol used for the esterification reaction was Merck-Schuchardt. The aliphatic dicarboxylic acids used for the preparation of diallyl esters were: (a) oxalic acid, (Merck-Schuchardt), (b) adipic acid, (Merck-Schuchardt), and (c) sebacic acid (Merck-Schuchardt).

A two-component acrylic resin (DA 100, ICI Ltd. U.K.) was selected for the preparation of crosslinked acrylic samples. The resin consists of poly(methyl methacrylate) powder accompanied with methyl methacrylate monomer. The powder contains excess free radical catalyst (benzoyl peroxide) which can be thermally decomposed and propagate polymerization. The crosslinking agent can be added, in the methyl methacrylate liquid, taking into consideration the mixing ratio required.

Another type of acrylic resin, the DP 300 (same origin as above), should be attractive for the experiments because of its quick cure. The selection of DA 100 is based on the fact that the data for crosslinked acrylics are mostly referred to resins of this class.

Besides the crosslinkers prepared, 1,4-butanediol dimethacrylate, (Merck-Schuchardt) was used in concentrations ranging from 1 to 10% on the monomer. Finally, diallyl phthalate (pract. Fluka A. G., Buchs S. G.) was also used.

Esterification Reactions

In all three cases a 1000-mL glass reactor with mechanical stirring was used, placed in a glycerin bath. The reaction mixtures were as follows: (a) allyl alcohol 200 g, oxalic acid 126 g, toluene 200 mL, calcium chloride 40 g; (b) allyl alcohol 200 g, adipic acid 146 g, toluene 200 mL, calcium chloride 15 g; (c) allyl alcohol 80 g, sebacic acid 100 g, toluene 100 mL, calcium chloride 10 g.

The use of calcium chloride, instead of concentrated sulfuric acid which is a typical esterification catalyst, was preferred because of the oxidation of allyl alcohol by sulfuric acid, resulting in stained products. The water was removed during the reaction by azeotropic distillation, and the esterification was continued until no more water was produced. The reaction product was then washed twice with 1000 mL of water, and, finally, the residual toluene was removed by distillation. The diesters were then stored in a cool place.

Crosslinked Samples Preparation

The crosslinkers prepared as previously described, as well as 1,4-butanediol dimethacrylate and diallyl phthalate, were added in the monomer of the acrylic resin used, at the concentrations listed in Table I. The curing process carried out according to the manufacturer's recommendations. The specimens prepared had the form of plates of about 1 mm of thickness.

Swelling Experiments

For swelling, chloroform was used as a solvent and the specimens were immersed. The suitability of chloroform results from the fact that it is a very

TABLE I
Acrylic Samples Crosslinked with Various Crosslinkers

Crosslinker	Concentration phr (w/w)	Sample presentation
None	0	A
1,4-Butanediol		
dimethacrylate	1	B
	2	C
	4	D
	5	E
	10	F
Diallyl phthalate	10	DAP
Diallyl oxalate	10	DAO
Diallyl adipate	10	DAA
Diallyl sebacate	10	DAS

good solvent for thermoplastic poly(methyl methacrylate). An additional reason for this selection is that the interaction parameter of the system poly(methyl methacrylate)–chloroform is known.

The sheet shaped samples were immersed in chloroform and weighed until equilibrium was reached. Because of the high volatility of the solvent, the swollen samples were placed in a ground neck flask before weighing.

Sorption Measurements

For the sorption measurements a 50% aqueous solution of ethanol was used. The specimens cut from the molded acrylic plates were rectangular in shape of 25 mm for each side. The temperature during the sorption measurements was kept at 30°C, and the sorbed amount of the mixture was determined by weighing.

RESULTS AND DISCUSSION

The results obtained from swelling experiments are presented in Table II, expressing polymer volume (v_0), volume of swollen polymer (v), and the ratio $v_2 = v_0/v$.

TABLE II
Swelling of Crosslinked Specimens in Chloroform at 25°C

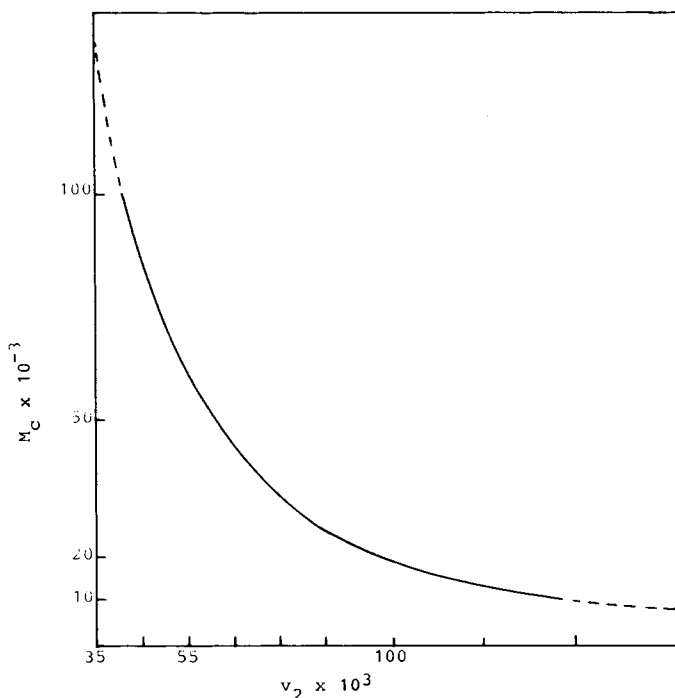| Specimen	v_0 (cm^3)	v (cm^3)	$v_2 \times 10^3$
B	0.49	6.36	77
C	0.52	5.3	98
D	0.6	5.5	109
E	0.55	4.9	112
F	0.48	3.12	154
DAP	0.61	8.12	75
DAO	0.62	12.4	50
DAA	0.62	4.6	135
DAS	0.59	4.8	123

Fig. 1.   Reference curve for the determination of M_c from swelling data.

The curve of Figure 1 is a useful tool for a quick approximation of the M_c values when the swelling ratio is known. This curve was derived by plotting the M_c values calculated by formula (1) using various values of v_2. It is obvious that the above curve is valid only for the system poly(methyl methacrylate)–chloroform, at 25°C. Concerning its reliability range (continuous line), the curve extends up to an upper limit of 100,000 M_c value because higher values are not possible, since the molecular weight of the linear poly(methyl methacrylate) itself is of the same order of magnitude. On the other hand, as a lower reliability limit one can recognize the M_c value of 10,000, since, thereafter, very small variations in M_c can result in considerable changes of swelling ratio. Because of this, only rough approximations can be obtained from Figure 1 for M_c value below 10,000 (dotted line).

The M_c values for different specimens shown in Figure 1 are plotted versus the crosslinker concentration in Figure 2. It is evident that crosslinking agent concentrations up to 4–5 phr by weight result in a limiting effect on the M_c, so that crosslink density increases slowly thereafter.

The M_c changes, as a function of the carbon atoms of the aliphatic chain (butanediol or diacids) used, are shown in Figure 3. It must be noted that M_c value is considered on the reference base of 1,4-butanediol dimethacrylate, i.e., each M_c value has been multiplied with M_b/M_x, where M_b the molecular weight of butanediol dimethacrylate (226) and M_x the molecular weight of the crosslinker under examination.

As Figure 3 indicates, the value of M_c is very sensitive to variations within the range of low carbon atoms values. The modified M_c values for 6 and 10
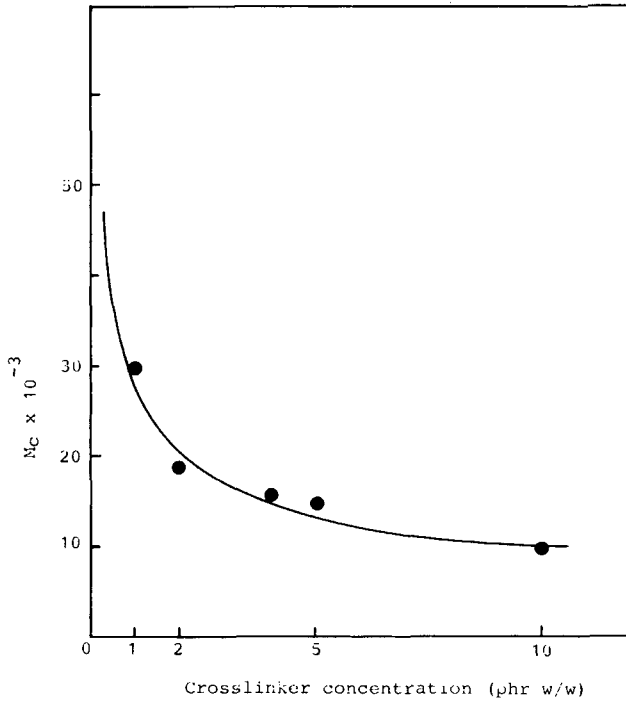
Fig. 2. M_c values as a function of crosslinker concentration.

carbon atoms seem to remain unaffected and the modified M_c value for 10 phr DAP equals about a 3 carbon atoms chain.

The sorption measurements, as an increase of weight of the specimens with immersion time, are presented in Table III. Furthermore, the sorption behavior expressed in terms of the ratio M_t/M_∞, where M_t = the weight of penetrant sorbed at time t and M_∞ = the weight of penetrant sorbed at equilibrium.
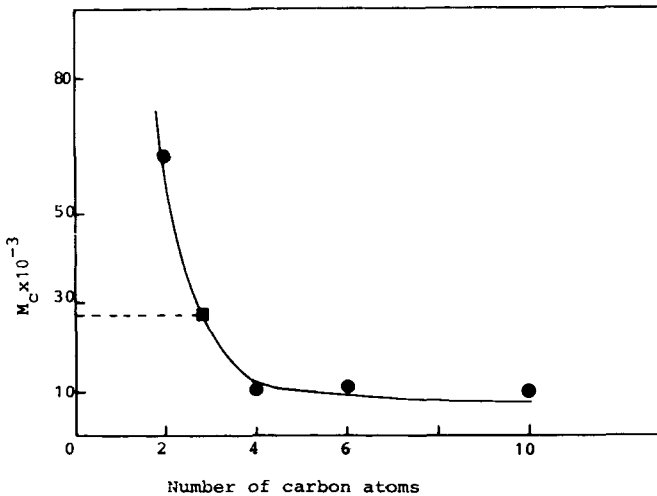

Fig. 3. M_c values as a function of carbon atoms in the aliphatic chain: (■) DAP.

TABLE III
Weight Increase for Specimens Immersed in 50% Ethanol at 30°C

| Spec.	Time (h):	Weight (g)									
		0	12	22	36	46	62	96	106	120	131
A		0.542	0.546	0.548	0.550	0.551	0.553	0.558	0.559	0.558	0.560
B		0.397	0.399	0.401	0.401	0.402	0.404	0.408	0.409	0.408	0.409
E		0.308	0.312	0.312	0.315	0.315	0.319	0.322	0.324	0.325	0.325
F		0.413	0.417	0.418	0.421	0.422	0.425	0.431	0.431	0.433	0.433
DAP		0.427	0.431	0.432	0.433	0.434	0.436	0.441	0.441	0.443	0.443
DAO		0.419	0.422	0.424	0.426	0.426	0.429	0.434	0.436	0.438	0.438
DAA		0.481	0.488	0.489	0.490	0.492	0.493	0.499	0.500	0.501	0.502
DAS		0.455	0.463	0.467	0.472	0.476	0.480	0.489	0.491	0.491	0.494
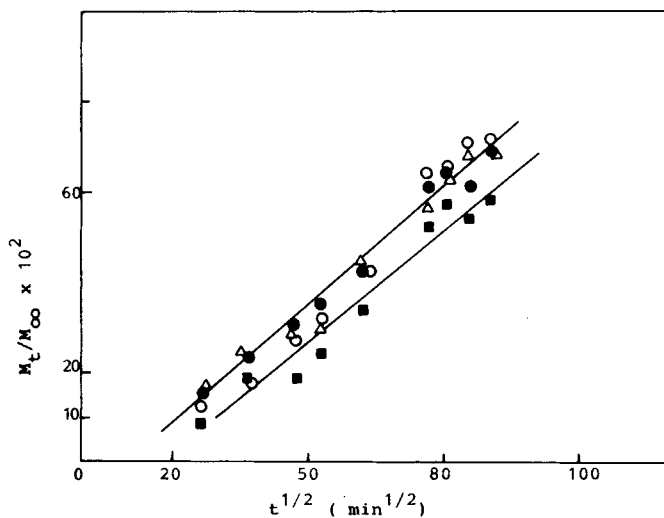
Fig. 4. Sorption of aqueous ethanol in various specimens, at 30°C: (●) A; (■) B; (△) E; (○) F.
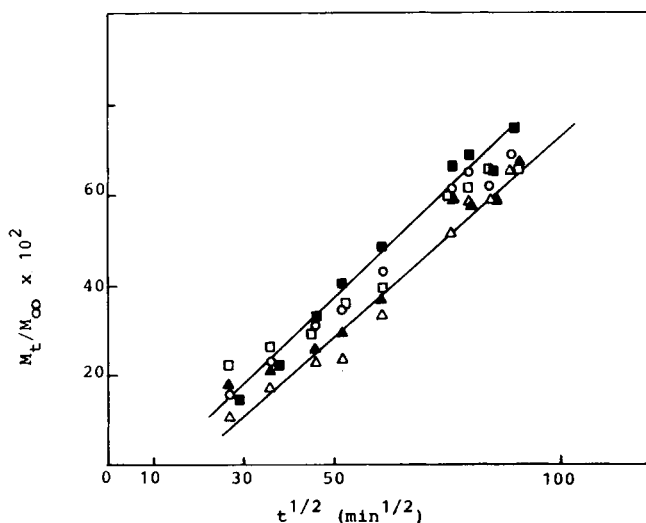

Fig. 5. Sorption in specimens crosslinked with various crosslinkers: (○) A; (▲) DAP; (△) DAO; (□) DAA; (▣) DAS.

The above ratio is plotted vs. $t^{1/2}$, for various crosslinker concentrations in Figure 4. Similar curves, for the other crosslinkers tested, are presented in Figure 5, in comparison with the unmodified poly(methyl methacrylate). As the curves of Figures 4 and 5 indicate, the sorption is Fickian in all cases, but no considerable change in the diffusion coefficient value is evident.

CONCLUSIONS

The results presented in the above study can lead to the following conclusions:

a. The esterification of aliphatic diacids with allyl alcohol is a simple process leading to crosslinking agents for vinyl polymers.

b. The versatility of diallyl esters allows crosslinked products to match the behavior of dimethacrylate crosslinked materials.

c. In general, long aliphatic chains give higher crosslinking efficiencies. A limiting effect is observed for 6 carbon atoms on the diacid chain.

d. Sorption measurements in aqueous ethanol cannot clearly distinguish the polymer networks derived by the use of various crosslinkers.

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