Chinese Chemical Letters Vol. 12, No. 11, pp 1029 – 1032, 2001
http://www.imm.ac.cn/journal/ccl.html

Cross-linking Copolymerization of Acrylic Acid and Multi-armed Cross-linkers

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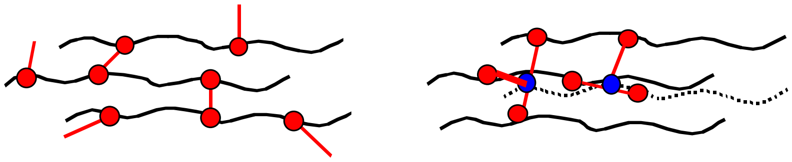
Abstract: The overall cross-linking copolymerization of acrylic acid and multi-armed cross-linkers are investigated by *in situ* interferometry. The results show that the more arms the cross-linkers have, the higher the polymerization rate is. However, they also mean the existence of less cross-linking efficiency and some defects in gel network.

Keywords: Multi-armed cross-linker, acrylic acid, *in situ* interferometry.

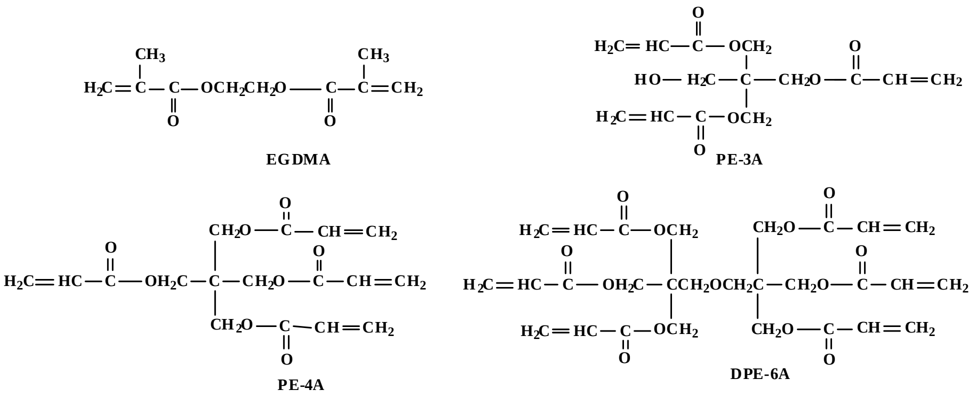
Polymer gels are of considerable interests in material science[1-3]. Many theoretical and experimental studies have been made on the cross-linking copolymerization[4-6] of these systems. Recently, *in situ* interferometry is applied in studying this process[7-9]. As shown in **Figure 1**, the common two-armed cross-linkers will lead to defects in the network, while multi-armed cross-linkers will enhance the integrity of the network. This paper studies the cross-linkers' influence on cross-linking and the integrity of the gel.

Figure 1 The network of gel cross-linked by two- and multi-armed cross-linker



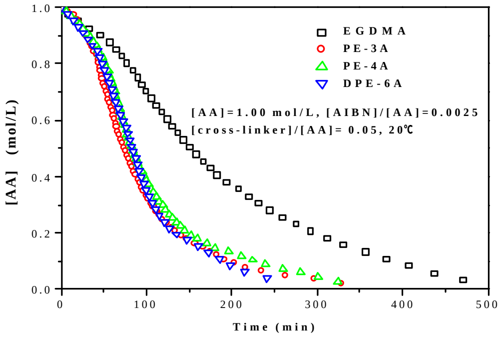
Polyacrylic acid gels(PAA) were synthesized in solvent $(CH_3)_2SO$ with AIBN as the photoinitiator. The influences of four kinds of cross-linkers, EGDMA, pentaerythritol-triacrylate (PE-3A), pentaerythritol-tetraacrylate (PE-4A) and dipentaerythritol-hexacrylate (DPE-6A), on the overall cross-linking copolymerization were studied in detail. The whole processes were recorded by *in situ* interferometry technique.

Figure 2 Molecular structures of the four cross-linkers



The exponent m, deduced from the equation[10] $Rp = k[I]^n [M]^m$, are 1.32, 1.20 and 1.21 for PE-6A, PE-3A, and EGDMA, respectively, when n is assumed as a constant. The similar constant m means similar polymerization mechanism or influence of cross-linkers on the decomposition of monomer free radical, especially at such low cross-linker level ([cross-linker]/[acrylic acid] = 0.005).

Figure 3 [Acrylic acid] changing with time in different cross-linkers system



However, the cross-linkers show different influence on the overall process even at the same concentration. The structures of the cross-linkers are similar, but the cross-linking groups or arms are different. That results different influence on the overall process. It is well known that the formed network will increase viscosity of the system, which suppresses the termination probability between two propagating chains and thus increases the polymerization rate[11]. This leads to an auto-acceleration stage of the polymerization system. The more arms the cross-linker has, the faster the gel network is formed. **Figure 3** shows the monomer is consumed slowly when EGDMA is used. The other three, PE-3A, PE-4A, DPE-6A, show similar effect on the process.

Detailed study on Rp shows that the double bonds in different cross-linkers are equally active. When the cross-linker concentration is as low as 0.003 mol/L or 0.005 mol/L, Rp descended in the order from DPE-6A to EGDMA (**Table 1**). In accordance with the classical assumptions that all double bonds in the cross-linker are equally active and react independently[12]. However, when the cross-linker concentration is relatively high, above assumption seems to be rejected. The Rp of PE-3A is higher than that of PE-4A when the cross-linker concentration is 0.03 mol/L. Furthermore, when the cross-linker concentration is 0.05 mol/L the order of Rp is almost reversed, PE-3A> PE-4A>DPE-6A>EGDMA.

F-Rp, shown in **Table 1**, is the fractioned Rp by the number of arms. It speeds up from EGDMA to DPE-6A at different concentration. The results suggest that the double bonds in different cross-linkers do not contribute the same effect on the formation of polymer network. The more arms the cross-linkers have, the less contribution of the double bonds to the cross-linking is. This is attributed to the intramolecular reaction of multi-armed cross-linker. That is to say, not all the double bonds in multi-armed cross-linker can contribute to the formation of the gel network

Table 1 Rp with different cross-linkers *

		[Cross-linker] : [AA]			
		0.003[a]	0.03[a]	0.005[b]	0.05[b]
Rp	DPE-6A	2.775	2.859	8.291	8.381
	PE-4A	2.165	2.231	7.704	9.309
	PE-3A	2.043	2.399	5.589	9.871
	EGDMA	-	-	4.269	4.365
F-Rp	DPE-6A	0.4625	0.4765	1.3818	1.3968
	PE-4A	0.5413	0.5578	1.7685	2.3273
	PE-3A	0.681	0.797	1.863	3.2903
	EGDMA	-	-	2.1345	2.1825

* : ([AIBN]/[AA]=0.0025 20°C),a: [AA]=0.60 mol/L, b: [AA]=1.00 mol/L

In this paper the equilibrium swelling ratio (R) is defined as the ratio of the weight of the absorbed water to the dried PAA gels at room temperature. Using PE-3A as cross-linker PAA gels had the lowest swelling ratio, no matter in higher or lower concentration (see **Table 2**). It is well known that the swelling of gel in water is determined by the topology structure of network. The more integrated the network is, the less swollen the gel is. Hence, the network of hydrogels using PE-3A as cross-linker is more integrated than other cross-linkers.

Table 2 Swelling ratio of PAA gels of different cross-linkers[a]

	DPE-6A	PE-4A	PE-3A	EGDMA
[DB-1]/[AA]=0.05	278.2	360.1	145	250.9
[DB-2]/[AA]=0.10	28.5	35.2	15.2	21.7

a: [AA]=1.00mol/L, [AIBN]/[AA]=0.0025

Acknowledgment

The National Natural Science Foundation of China (Grant No. 29774036, 59773019 and 29904007) and PPLAS Foundation of the Chinese Academy of Sciences are acknowledged for their financial supports. The discussions among International Center of Polymer Gel are helpful to this paper, especially that with Dr. Mingming Guo (Univ. of Akron), Dr. Zhibing Hu (Univ. of North Texas).

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Received 2 April, 2001