

# Inhibition of Radical Polymerization in Solvent-Based Systems (Security of Solvent-Based Radical Polymerization of PSA-Acrylic in a Plant Reactor)

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**ABSTRACT:** This article shows the influence of some chain-transfer agents as inhibitors for acrylic solvent-based polymerization. These chain-transfer agents can offer significant advantages, as outlined below. The following chain-transfer agents were studied to stop or slow down the polymerization process in the case of a runaway: *n*-dodecyl mercaptan, trimethylolpropane-trimercaptoacetate, phenothiazine, diphenylphenylen diamine, cuprum oxide, isopropanol, toluene, and carbon tetrachloride. Synthesized

pressure-sensitive adhesive based on acrylic polymers and containing 2-ethylhexyl acrylate, methyl acrylate, and acrylic acid were used for the production of self-adhesives with high cohesion. The polymerization was accomplished in ethyl acetate. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1354–1357, 2003

**Key words:** polymerization; acrylic polymers; molecular mass; viscosity

## INTRODUCTION

The markets and technology for high-performance acrylic pressure-sensitive adhesives are expanding rapidly. The growing market is the result of expansion in both current and new application areas. The ever-changing high-performance pressure-sensitive acrylic adhesive market continues to expand and present new challenges. The target of this study was to find and test inhibitors for the solvent polymerization process in the production of pressure-sensitive adhesives based on acrylates. In the case of danger (e.g., runaway), the polymerization process must be stopped or slowed down to guarantee the security of reactor in the production plant. Cooling of the reactor in the production plant is widely used; however, in the case of cooling-system failure, inhibitors should be easily available.

Modification to control the molecular mass and molecular mass distribution is necessary so that the resulting polymers have good processibility and other properties required for their intended application.

Chain-transfer constants are an index to the efficiency of chain transfer agents in certain free-radical polymerization systems. The chain transfer constant "C" is defined as

$$C = \frac{\text{reaction rate constant of the transfer reaction}}{\text{reaction rate constant of the propagation reaction}}$$

Mayo<sup>1</sup> has developed the following equation relating the chain transfer constant to the degree of polymerization

$$\frac{1}{P} = C \frac{(S)}{(M)} + \frac{1}{P_0}$$

where *P* is the degree of polymerization in the presence of a chain-transfer agent; *P*<sub>0</sub> is the degree of polymerization in the absence of a chain-transfer agent; (*S*) is the concentration of chain-transfer agent; and (*M*) is the concentration of the monomer.

## EXPERIMENTAL

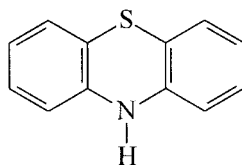
The following experiments were performed to study the influence of diverse inhibitors to stop or slow down the polymerization process of pressure-sensitive acrylic adhesives in the case of a runaway in the manufactory plant. The basic pressure-sensitive adhesive (PSA) acrylic was synthesized with 60% 2-ethylhexyl acrylate (2-EHA), 20% methyl acrylate (MA), 15% ethyl acrylate (EA), and 5% acrylic acid (AA) by polymerization in the presence of azobisisobutyronitrile (AIBN) in a typical organic solvent such as ethyl acetate.<sup>2</sup> The solid content during the polymerization was 50 wt %. For the most efficient inhibitors, the change of concentration of nonreacted monomers during inhibition, was studied. Molecular mass and solvent viscosity of acrylic PSA were measured by using different concentrations of the most efficient studied inhibitors (0.025–0.5% w/w).

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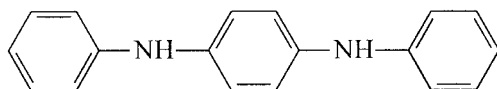
2-EHA, MA, EA, AA, AIBN, ethyl acetate, isopropanol, toluene, and carbon tetrachloride were purchased from Tokyo Chemical Industry Co. (TCI) (Tokyo, Japan).

Others initiators, dodecyl mercaptan (DDM) and trimethylolpropane-trimercaptoacetate (TTMA), were purchased from Bruno Bock Chemische Fabrik (Mannheim, Germany) Germany and phenothiazine (PTZ), diphenylphenylen diamine (DPPD), and cupric oxide ( $\text{Cu}_2\text{O}$ ) were purchased from Merck (Darmstadt, Germany).

The inhibitors used in this work are shown below:



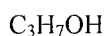
phenothiazine (PTZ)



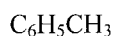
diphenylphenylen diamine (DPPD)



cuprum oxide (solved in methanol)



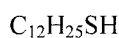
isopropanol



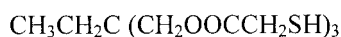
toluene



carbon tetrachloride



dodecyl mercaptane (DDM)



trimethylpropane-tri-mercaptopoacetate (TTMA)

until now, yielded a list of 132 articles.<sup>3-5</sup> The most relevant publications are listed in the references.

In the first step, exactly 1 wt % of the inhibitor was added during the synthesis of PSA acrylic short after the polymerization was initiated (foam maximum level). The basic PSA acrylic consisted of 60% 2-EHA, 20% MA, 15% EA, and 5% AA. The solvent was ethyl acetate and the solid content was 50% w/w.

Small, solvent-based PSA samples were taken from the reaction mixture during the polymerization process (reference), just before and just after addition of the inhibitor. The first measurements were started after 45 min, approximately at the moment, whereas on the polymeric surface in the reactor, foam could be observed that shows high exothermicity of the polymerization.

The free-monomer content was measured by GC in the analytical laboratory to check if the inhibition was effective. The foam level during the polymerization and foam after addition of the inhibitor were visually observed.

## RESULTS AND DISCUSSION

The free-monomer (residual monomer) content and the time of maximum level of foam are shown in Table I. The samples were taken from the reactor after the time specified in Table I. The measurements were started once the polymerization was initiated.

The graphic diagram (Fig. 1) shows the change in the amount of free monomers during the polymerization reaction.

Trimethylpropane-trimercaptoacetate (TTMA) was the best inhibitor of polymerization. The inhibitor was tested in the next experimental setting where the concentration of the nonreacted monomers was measured. The results are shown in Table II.

In Figure 2, the amount of free monomers for each acrylate in the case of the best inhibitor (TTMA) is presented.

The following remarks can be made regarding the course of polymerization with the tested inhibitors.

- The time of maximum level of foam during the polymerization reaction of acrylate monomers was between 51 and 56 min.
- Once the polymerization is started (the time of maximum level of foam), it is impossible to stop it; however, the process can be slowed down so the danger in the plant is significantly reduced.
- The best inhibitor was TTMA.
- Very good results were achieved by cooling the reactor. The level of free monomers after foam decreasing was the same as after the cooling of the reaction system. During later cooling, no more free radicals were created.

A literature search "Inhibition of polymerization of acrylic monomers," covering the period from 1972

**TABLE I**  
Overview of the Amount of Free Monomers and Time of Maximum Level of Foam during the Polymerization with Inhibition

Inhibitor	Time of maximum level of foam	Concentration of free acrylic monomers [%] during the polymerization after ... (min)							
		45	50	55	60	65	70	90	120
Reference	56	23.5	22.4	22.1	20.8	18.6	15.9	11.9	8.3
With cooling	55	24.1	22.3	21.8	19.9	19.8	19.9	20.1	20.0
PTZ	51	23.1	22.3	21.8	20.7	20.4	19.8	19.8	17.8
DPPD	52	23.2	21.4	21.1	20.9	20.7	20.5	20.0	19.5
Cu <sub>2</sub> O	53	22.6	21.2	20.2	18.6	18.5	18.1	17.0	13.5
C <sub>3</sub> H <sub>7</sub> OH	55	23.2	22.5	21.9	20.6	18.1	15.6	12.3	8.3
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	53	24.2	22.8	22.4	21.8	21.0	20.5	19.0	17.1
CCl <sub>4</sub>	52	24.0	23.0	22.5	21.8	21.1	20.4	19.4	18.0
DDM	54	24.4	23.0	21.5	21.1	20.7	20.4	20.2	20.0
TTMA	56	24.0	22.5	21.2	21.0	20.8	20.5	20.4	20.4

- Good results were achieved with phenothiazine (PTZ).
- The results with isopropanol, Cu<sub>2</sub>O, and toluene were worse than with PTZ.
- The remnants of free monomers measured with mercaptans as DDM and TTMA revealed very similar values.
- When TTMA as polymerization inhibitor was used, the different reactivity of the acrylates was demonstrated (Fig. 2). The reactivity order was

methyl acrylate > ethyl acrylate > 2-ethylhexyl acrylate.

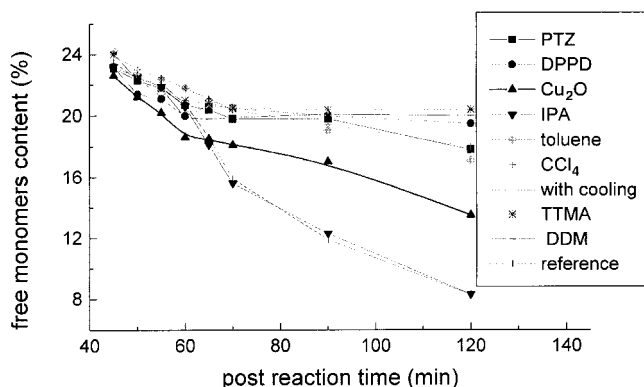
- Free acrylic acid was not noticed, which confirms its high reactivity.

In the case of the best transfer agent TTMA, the molecular mass and the solution viscosity of tested PSA were measured (Table III).

As shown in Table III, the transfer agent TTMA has a strong effect on the molecular mass reduction (Fig. 3) and also on viscosity (Fig. 4).

The following remarks can be made regarding the course of polymerization with TTMA:

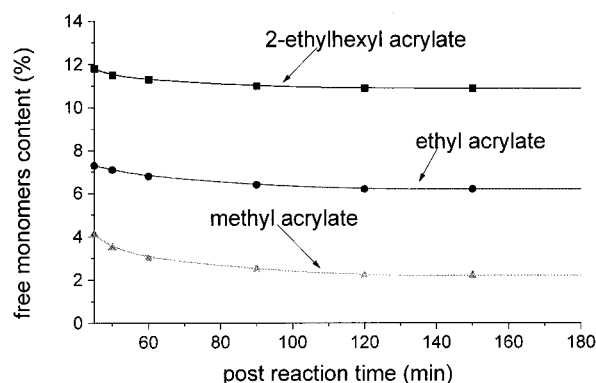
- The linear increase in the concentration of TTMA produced a hyperbolic decrease of molecular mass and solution viscosity of synthesized PSA.
- Overdosing of TTMA (above 0.05% w/w) decreased the molecular mass of PSA to a level where the resultant molecular mass may not provide high cohesion of the PSA.
- A too strong decrease of the solution viscosity may lead to problems related to coating on critical non adhesive surfaces.



**Figure 1** Effect of post reaction time on free monomers with diverse inhibitor systems.

**TABLE II**  
Free Acrylic Monomers during the Polymerization with TTMA

Time (min)	Monomers content (wt %)		
	2-EHA	EA	MA
45	11.8	7.3	4.1
50	11.3	6.7	3.5
60	10.9	6.4	2.5
90	10.8	6.3	2.3
120	10.8	6.3	2.3
150	10.8	6.2	2.3
180	10.8	6.2	2.3



**Figure 2** Effect of post reaction time on each free acrylic monomer content by use of TTMA.

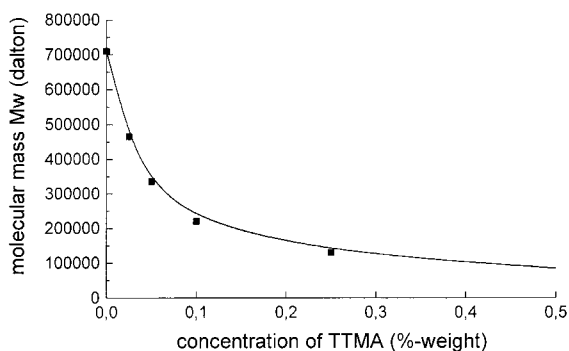
**TABLE III**  
Molecular Mass and Solution Viscosity by Use of TTMA

TTMA (wt %)	$M_w$ of polyacrylate (Da)	Solution viscosity [m Pas]
0	710,000	8500
0.025	465,000	3000
0.050	335,000	2100
0.10	220,000	1410
0.25	130,000	810
0.50	85,000	635

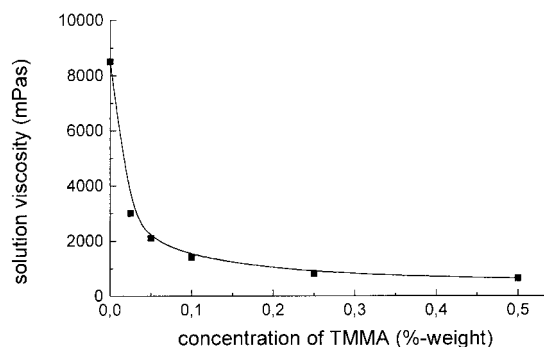
A molecular weight of 300,000 Da is known as a practical lower limit of PSA with high cohesion. The adhesives with higher molecular mass presented very good physical and mechanical properties. PSA with molecular mass below 300,000 Da did not meet the criteria even after crosslinking and thus may not be used in production.

### CONCLUSIONS

- TTMA was the best inhibitor leading to reduction of residual monomers.



**Figure 3** Molecular mass of PSA dependence of TTMA concentration.



**Figure 4** Solution viscosity of PSA dependence of TTMA concentration.

- TTMA and PTZ were the best inhibitors leading to a decrease in foam.
- The best way to secure polymerization of a blend of monomers in polymerization reactor in the plant is the use of TTMA with cooling of polymerization reactor.
- TTMA may be effectively used as a transfer agent for the regulation of molecular mass of the synthesized acrylic PSA from different monomers.
- TTMA as a transfer agent gives the possibility of unlimited regulation of molecular weight and of solution viscosity of the synthesized acrylic PSA.

### References

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