ACCELERATING RATE CALORIMETRY OF MONOMERS ON ABSORBENTS

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Summary

A study of the polymerization of a number of monomers and a variety of known absorbents has been carried out using the technique of accelerating rate calorimetry. Monomers chosen for the study were styrene, vinylidene chloride, ethyl acrylate, methyl acrylate, butyl acrylate, and methyl methacrylate. The absorbents tested were Zorb-all, vermiculite, Safestep, and Slikwik and Lite-R-Cobs ground corn cobs. The data indicate that styrene, methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate exhibit accelerated polymerization when in the presence of Zorb-all at elevated temperatures compared to the neat monomers under conditions of the experiment.

Introduction

The study of thermal hazards associated with the manufacture, transport, storage, and other handling of reactive chemicals is an active area of research in the chemical industry. Whenever quantities of chemicals are moved, the potential exists for some type of spill to take place. It is, therefore, important to investigate the potential hazards associated with the cleanup of such spills.

Without proper controls, monomers can undergo polymerizations which may result in large temperature rises and hazardous situations. Such runaway polymerizations of monomers on absorbents are dependent on factors such as temperatures of materials, thermal initiation, catalytic initiation, heat transfer, vaporization of monomers, etc. Generally, small amounts of monomer-saturated absorbents exhibit little potential for runaway polymerizations since heat transfer out of the material is usually rapid relative to the rate of heat generation. For large amounts of monomer-saturated absorbents, however, the rate of heat generation may be larger than the rate of heat loss, resulting in a runaway polymerization.

The accelerating rate calorimeter (ARC) cannot directly simulate runaway polymerizations of large amounts of monomer saturated at ambient tem-

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perature conditions. ARC can, however, be used to examine the relative stability of monomers in the presence of absorbents at elevated temperatures. Monomers chosen for the study were styrene, vinylidene chloride, methyl acrylate, ethyl acrylate, butyl acrylate, and methyl methacrylate (all production grade). The absorbents tested were Zorb-all (product of International Minerals and Chemical Corporation), vermiculite, Safestep (product of Andesite of California, Inc.), Slikwik ground corn cobs (product of The Andersons, Cob Division), and Lite-R-Cobs (product of The Andersons) which was used with styrene.

Experimental

The technique used to test the monomer/absorbent systems was accelerating rate calorimetry (ARC). ARC has been used in the past to investigate the thermal stabilities of materials [1, 2]. The samples were either run in the standard heat—wait—search mode, or were isothermally aged for a specific length of time before heat—wait—search in order to destroy part of the inhibitor in the monomer. Temperature and length of time for aging were chosen so that the system would enter exotherm while laboratory personnel were present. This was necessary because the slopes of the heat-rate curves for the acrylates were high, and part of the exotherm could be missed in the normally unattended ARC running mode. See Appendix I for specific experimental conditions for each of the runs. Samples were run in 1 in. diameter Hastelloy C holders under air atmosphere. The exotherm detection threshold was 0.02°C/min (see Ref. [3] for general operating procedures for ARC). Volume ratio of monomer to absorbent was approximately 1:1, which yielded surface wet sample with adequate thermal conductivity for the ARC experiment.

Results

There are a number of factors that make it difficult to predict the absolute stability of an inhibited monomer system. These factors include the type of inhibitor used, the concentrations of the inhibitor in the monomer and the monomer on the absorbent, oxygen concentration, the number of possible polymerization mechanisms, and wall effects in the 1 in. diameter sample holder. In an effort to eliminate some of these factors, we have tried to run the experiments under similar conditions and have compared the relative stabilities of each of the monomer systems. It should be noted that these results apply to elevated temperatures and may not necessarily apply to systems at room temperature.

The self-heat rate curves for a specific monomer have been plotted on the same graph for the purpose of easy comparison. The graphs for styrene, vinylidene chloride, methyl acrylate, ethyl acrylate, butyl acrylate and methyl methacrylate may be found in Figs. 1, 2, 3, 4, 5, and 6, respectively.

The thermal ratio, ϕ, is defined as:

$$\phi = \frac{M_s C_{vs} + M_b C_{vb}}{M_s C_{vs}}$$

where M_s is the sample mass, C_{vs} is the specific heat of the sample at constant volume, M_b is the container mass, and C_{vb} is the specific heat of the container at constant volume.

ϕ is a measure of the adiabaticity of the sample for the special case where a thermal steady-state exits between the sample and its container at all times [1]. Before comparison of the ARC data, it is necessary to calculate the relative ϕ values for the individual runs. For a given chemical reaction, as the thermal inertia is increased, the experimental temperature rise is observed to decrease (see Ref. [1] for a discussion of the effect of ϕ on observed ARC curves for styrene polymerizations).

Table 1 is a summary of the ϕ data for all of the experimental runs. The ϕ factors have been adjusted to add the mass of the absorbent (M_a) times the specific heat of the absorbent at constant volume (C_{av}) (estimated to be 0.22 cal/g °C for Zorb-all, vermiculite and Safestep, and 0.32 cal/g °C for Slikwik*) to that of the container, considering the absorbent as non-reacting component of the system.

TABLE 1

ϕ Factors[a] for the individual ARC runs

Sample	Monomer	Zorb-all	Vermiculite	Safestep	Corn Cobs
Styrene	1.47	2.37	1.93	2.16	1.79
Vinylidene chloride	1.97	2.24	2.16	2.23	2.03
Methyl acrylate	2.24	2.59	2.37	2.71	2.48
Ethyl acrylate	2.17	2.40	2.28	2.61	2.52
Butyl acrylate	2.99	3.38	3.34	3.10	3.25
Methyl methacrylate	2.25	2.65	2.40	2.60	2.57

[a] $\phi = (M_s C_{vs} + M_b C_{vb} + M_a C_{va})/M_s C_{vs}$, where M_s, C_{vs}, M_b, C_{vb}, M_a, and C_{va} are as defined in the text. The mass of the sample is that of the monomer only.

The adiabatic temperature rise, ΔT_{ab}, calculated from the product of the temperature rise (final exotherm temperature minus initial exotherm temperature) and the ϕ value, is found in Table 2. There is no entry for vinylidene chloride because the exotherms were not complete by 250°C (the experimental pre-set end temperature) and dehydrochlorination may occur above 150°C. The ΔT_{ab} can be used as an indication of the consistency

*Based on specific heat values from the Chemical Engineers Handbook, where the value for clay is given as 0.22 cal/g °C and for cellulose as 0.32 cal/g °C.

TABLE 2

Adiabatic temperature rise, ΔT_{ab} (°C)

Sample	Monomer	Zorb-all	Vermiculite	Safestep	Corn Cobs
Styrene	260	226	204	274	286
Methyl acrylate	290[a]	328[a]	302[a]	376	360
Ethyl acrylate	320[a]	358[a]	284[a]	220	356
Butyl acrylate	218[a]	256[a]	208[a]	190[a]	264[a]
Methyl methacrylate	175	204	152	162	314

[a]These data are not corrected for heat losses which may occur at self-heat rates exceeding 10°C/min. The ΔT_{ab} values may be too low for this reason.

of the data. If the system were adiabatic and the assumed specific heats representative, the ΔT_{ab} values would be similar for a specific monomer system.

The self-heat rate curves presented in this paper are not corrected for ϕ effect since this correction would require knowledge of true kinetics of polymerization. Direct comparisons of self-heat rate curves should not be made unless the thermal ratios are the same.

For styrene, Fig. 1, the polymerization with Zorb-all began ~20°C below that of the other systems. Thermal polymerization of styrene in the presence of other absorbents did not differ significantly from that of styrene mon-
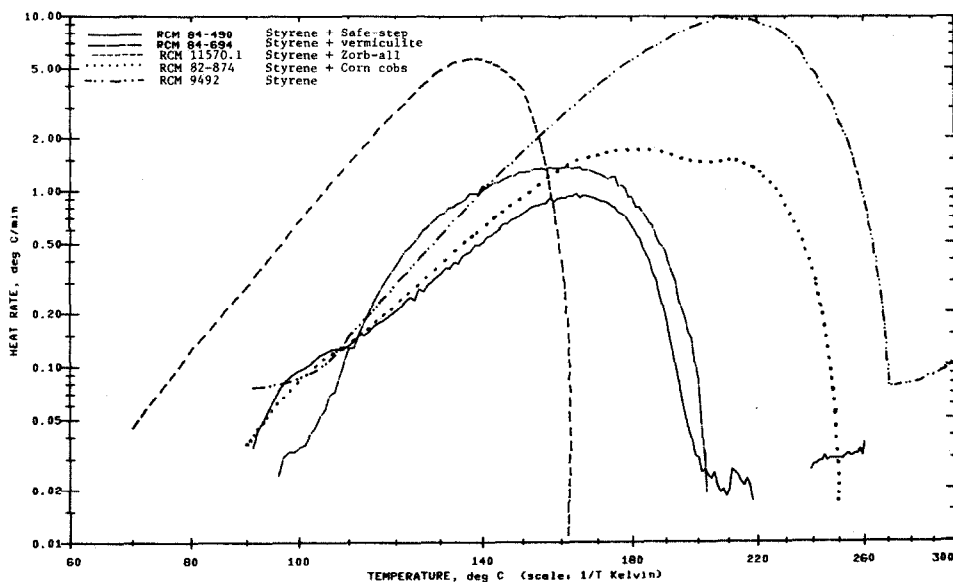

Fig. 1. Self-heat rate curves of styrene monomer and styrene on absorbents (sample weight 4.650 g).
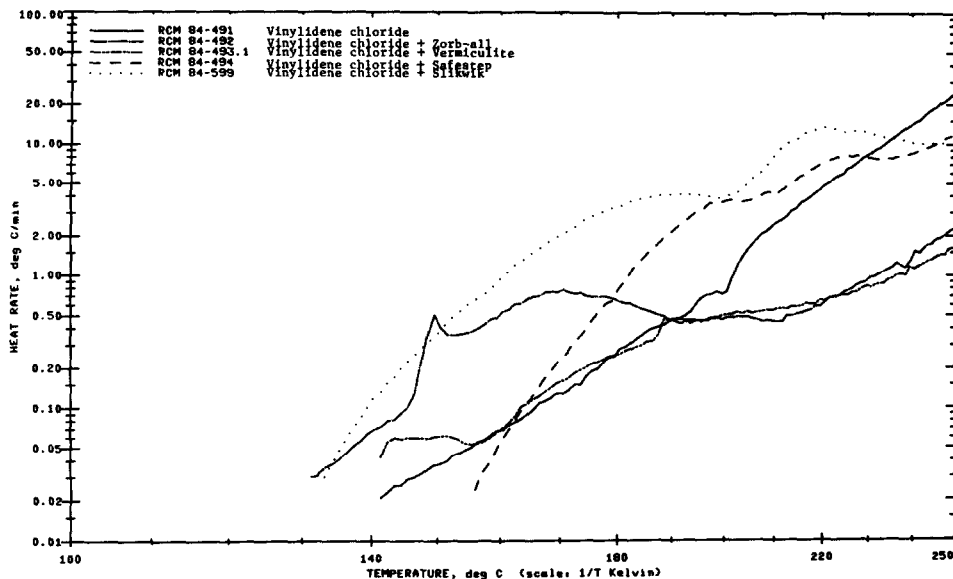
Fig. 2. Self-heat rate curves of vinylidene chloride monomer and vinylidene chloride on absorbents (sample weight 3.910 g).

omer. They did exhibit a decrease in temperature rise as the ϕ factors increased, as seen by the reasonable consistency of the ΔT_{ab} data of Table 2.

The vinylidene chloride (VDC) plots are in Fig. 2. It did not appear that there was any drastic difference in the self-heat rate curves for vinylidene chloride with any of the absorbents tested (relative to the hazards associated with the pure monomer system). There was an indication in the vermiculite plot that the interaction with VDC was somewhat different from that of VDC with the other absorbents. The initial slope was much smaller for vermiculite than for the other systems. Other experiments indicated that this slow exothermic activity may be detected at temperatures as low as 140°C.

Figure 3 contains the methyl acrylate self-heat rate curves. It is seen that in terms of exotherm start, the Zorb-all had the lowest onset temperature. Vermiculite and Safestep had little effect on the exotherm onset temperature. The ground corn cobs increased the exotherm onset temperature compared with the neat monomer. The ΔT_{ab} values were reasonably consistent for all of the runs.

The ethyl acrylate plots are seen in Fig. 4. Compared with the monomer, the Zorb-all and Slikwik systems initiated at lower temperatures (132°C and 143°C, respectively, compared to 151°C for the monomer). Only the Safestep sample initiated at a higher temperature (191°C). The ΔT_{ab} values were approximately the same, with the Safestep sample the lowest.

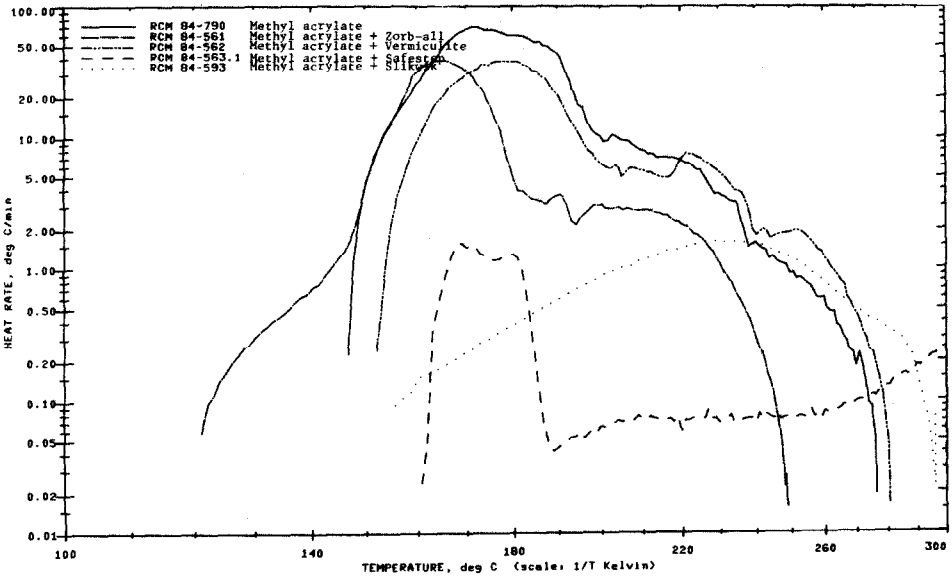The butyl acrylate plots are found in Fig. 5. The only absorbent that

Fig. 3. Self-heat rate curves of methyl acrylate monomer and methyl acrylate on absorbents (sample weight 3.020 g).
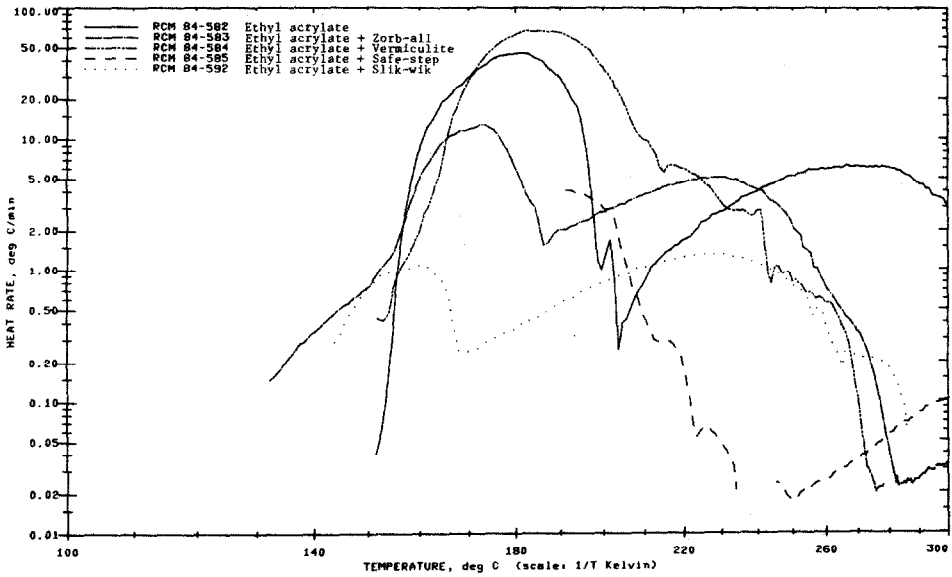

Fig. 4. Self-heat rate curves of ethyl acrylate monomer and ethyl acrylate on absorbents (sample weight 3.250 g).
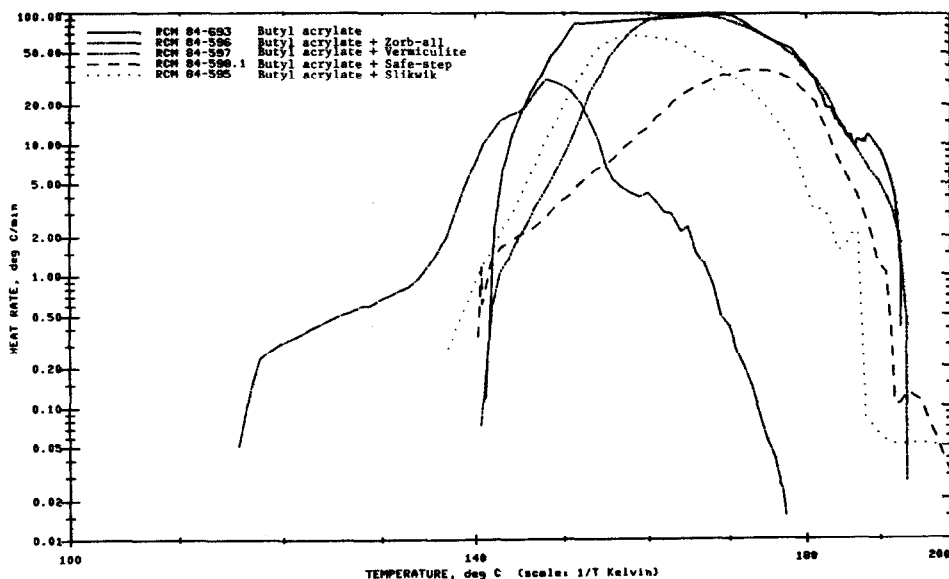
Fig. 5. Self-heat rate curves of butyl acrylate monomer and butyl acrylate on absorbents (sample weight 1.920 g).

caused a significantly different self-heat rate curve compared with the monomer was that of Zorb-all. Exotherm onset temperature of this system was 115°C compared with 140°C for butyl acrylate monomer. The ΔT_{ab} values for all of the systems were consistent, ranging from 190°C for Safestep to 246°C for Slikwik.

Figure 6 is the graph for the methyl methacrylate system. With the exception of Zorb-all, results using the other absorbents showed higher exotherm onset temperatures than the monomer (116°C for the monomer, 125°C for vermiculite, 128°C for Safestep, and 120°C for Slikwik). Zorb-all initiated at 100°C, ~20°C lower than the monomer.

One possible explanation of the difference in behavior between Zorb-all and vermiculite or Safestep may be in the heat treatment of the material. Vermiculite is normally heated to 500—700°F, which causes expansion and eliminates the water from the system [4]. Safestep is described as an inert, inorganic blend of siliceous and other minerals insoluble in practically all solvents and strong mineral acids, except hydrofluoric acid. It is possible that Safestep is a calcined clay like Zorb-all. Clays are normally calcined at ~1100°F [4]. We decided to heat Zorb-all to ~1000°C for about two hours to see the effect of this extreme heat treatment on the exotherm onset temperature for styrene polymerization on treated Zorb-all. It was found that there was little change in the onset temperature for the treated Zorb-all (63°C) as compared with the untreated (68°C), eliminating differences in heat treatment as a likely explanation for the phenomenon.
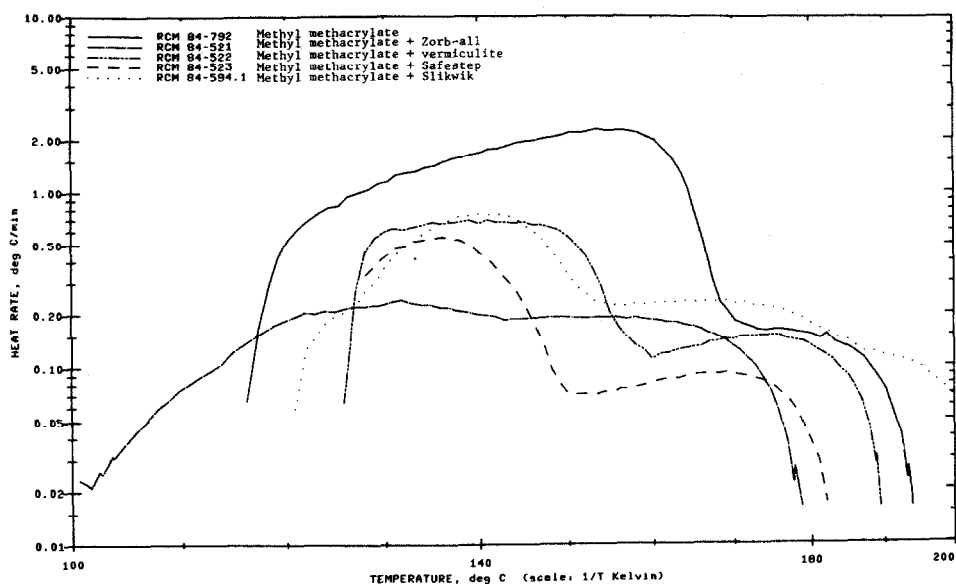
Fig. 6. Self-heat rate curves of methyl methacrylate monomer and methyl methacrylate on absorbents (sample weight 3.040 g).

As both Zorb-all and vermiculite are expected to have high cationic exchange abilities [4], cationic activity alone would not account for the lower onset temperature with Zorb-all. An ionic absorbent, DOWEX (trademark of The Dow Chemical Company) MSC-1 resin, was also tried with styrene. The onset temperature was 81°C, which was lower than vermiculite and Safestep by 10—15°C, but still higher than Zorb-all by 15°C. Styrene on molecular sieves 4A was similar to the styrene monomer in exotherm onset temperature.

It is also possible that the catalytic effect is related to metallic elements in the inorganic structures or to specific activity on the surface as compared with the interior of the absorbent.

Conclusion

The data indicate that styrene, methyl acrylate, ethyl acrylate, butyl acrylate, and methyl methacrylate exhibit accelerated polymerization when in the presence of Zorb-all at elevated temperatures compared with the neat monomers under conditions of the experiment. Although vermiculite, Safestep, and Slikwik (and Zorb-all in vinylidene chloride) did not appear to accelerate the polymerization of the monomers, this is not a guarantee that a runaway polymerization could not occur. Large piles of solid absorbents containing monomer could be sufficiently self-insulating so as to keep most of the heat generated during a very slow polymerization. Large spills should, therefore, be handled carefully after absorbing the monomer.

Acknowledgments

References

1 L.F. Whiting and J.C. Tou, J. Therm. Anal., 24 (1982) 111—132.
2 J.M. Pickard, J. Hazardous Mater., 7 (1983) 291—302.
3 CSI-ARC Manual, Columbia Scientific Industries, Austin, Texas.
4 McGraw-Hill Encyclopedia of Science and Technology, McGraw-Hill, New York, NY, 1982: Vol. 2, pp. 195—196; Vol. 3, pp. 229—233; Vol. 8, pp. 735—736; Vol. 14, pp. 387—388.

Appendix I

Experimental conditions for sample aging

Sample	Aging time (h)	Start temperature (°C)
Styrene		
Monomer	No	50
Zorb-all	No	30
Vermiculite	6	60
Safestep	No	30
Lite-R-Cobs	No	30
Vinylidene Chloride		
Monomer	6	80
Zorb-all	6	60
Vermiculite	6	80
Safestep	6	60
Slikwik	6	60
Methyl acrylate		
Monomer	6	80
Zorb-all	6	80
Vermiculite	6	80
Safestep	6	80
Slikwik	6	80
Ethyl acrylate		
Monomer	10	80
Zorb-all	6	80
Vermiculite	6	80
Safestep	8	80
Slikwik	6	80

Butyl acrylate

Monomer	10	80
Zorb-all	10	80
Vermiculite	10	80
Safestep	No	135
Slikwik	10	80

Methyl methacrylate

Monomer	6	60
Zorb-all	6	60
Vermiculite	6	60
Safestep	6	60
Slikwik	6	60