

Free Radical Polymerization of Nitropropyl Acrylates and Methacrylates. I. Heat of Polymerization

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ABSTRACT: The heat of polymerization ΔH_p , of nitropropyl(meth)acrylate monomers has been studied by differential scanning calorimetry (DSC) in dynamic and isothermal modes. DSC showed that ΔH_p of 2-nitropropyl(meth)acrylate was surprisingly smaller than that of propyl(meth)acrylate but similar to that of 2,2-dinitropropyl(meth)acrylate. According to molecular structure analysis by a PM3 Hamiltonian in a MOPAC program, the contributing main factor to the lowering of ΔH_p of 2-nitropropyl(meth)acrylate was found to be the hydrogen bond between the O(=C) and the H atom attached at position C6. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2929–2935, 2001

Key words: heat of polymerization; nitropropyl(meth)acrylate; molecular structure analysis; PM3 Hamiltonian in a MOPAC program; hydrogen bond

INTRODUCTION

The heat of polymerization, ΔH_p is a dominating component in constituting the molar free energy of a compound. It is a driving force for the propagation reaction, which governs the rates and kinetics of polymerization. The accurate measurement of thermochemical data on heats of polymerization is of importance because of (1) basic knowledge of the driving force for the propagation reaction, and (2) better understanding of the molecular structure of the monomers during polymerization.¹

A number of studies have been carried out on the measurement of heat of polymerization of vinyl monomer with various methods, such as calorimetry. Among calorimetries, differential scanning calorimetry (DSC) has been used with success to follow the course of free radical poly-

merization with bulk monomer using either an isothermal or a dynamic method.^{2–6}

Nitroalkyl acrylate polymers have been studied as the energetic binder in the field of propellants and explosives.^{7,8} Among them, 2,2-dinitropropyl acrylate (DNPA) polymer has been applied to the plastic bonded explosive (PBX). However, kinetic and calorimetric studies on free radical polymerization of DNPA monomer are scarce, nor have any enthalpic studies of this reaction been reported.

The goal of the present DSC study is to add to the existing knowledge on the free radical homopolymerization of DNPA in bulk and also determine the effects of the nitro group on heats of the polymerization of propyl(meth)acrylate containing one or two nitro groups.

EXPERIMENTAL

Materials

Preparation of 2-Nitropropanol⁹

To a mixture of 230 g (3.06 mol) of nitroethane and 500 mL of distilled water was slowly added

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50% NaOH aqueous solution at a temperature just below 10°C until achieving an aqueous solution with a pH value of 9. After 30 min, the solution was heated to room temperature. To the solution was poured 289 g (3.37 mol) of 35% aqueous formaldehyde solution, and acetic acid was added to solution until achieving a solution with a pH value of 5. The product was extracted four times from the aqueous solution with 300 mL of methylene chloride. The methylene chloride layer was washed with 300 mL of saturated NaCl aqueous solution and with 300 mL of distilled water and dried with magnesium sulfate. After methylene chloride was evaporated, 131 g (41% of yield) of 2-nitropropanol of greater than 96% of purity was obtained.

Preparation of 2,2-Dinitropropanol¹⁰

To a mixture of 31.28 g (0.4 mol) of nitroethane and 80 mL of distilled water was slowly added 35.2 g (0.44 mol) of 50% NaOH aqueous solution at a temperature just below 10°C; 30.84 g (0.44 mol) of solid NaNO₂ was added. In 400 mL of distilled water was dissolved 135.9 g (0.88 mol) of AgNO₃ at 0°C. To the nitroethane solution was poured AgNO₃ aqueous solution. The solution immediately became dark green with precipitation of silver. After 2 min, the solution was heated to room temperature; 50% NaOH aqueous solution was slowly added until achieving a solution with a pH value of 12 at a temperature just below 20°C. The solution was pale red after silver was filtered. To the filtrated solution was added acetic acid until achieving a solution with a pH value of 9 at room temperature. To the solution was poured 41.18 g (0.48 mol) of 35% formaldehyde aqueous solution. Finally, 100% acetic acid was added until achieving a solution with a pH value of 5. The product was extracted three times from the aqueous solution with 300 mL of methylene chloride. The methylene chloride layer was washed with 300 mL of saturated NaCl aqueous solution three times and 300 mL of distilled water. Methylene chloride solution was dried with magnesium sulfate. After methylene chloride was evaporated, 52.3 g (87% of yield) of 2,2-dinitropropanol with above 97% of purity was obtained.

Preparation of Nitropropyl Acrylates and Methacrylates¹¹

In a typical preparation, DNPA was prepared as follows. A solution of 75 g (0.5 mol) of 2,2-dinitropropanol, 39.6 g (0.55 mol) of acrylic acid, 150 g

Table I Reaction of Corresponding Acrylic Acids and Nitroalcohols

Monomer	Alcohol (mole)	Acid (mole)	Solvent (mL)	Catalyst (g)	Temp (°C)	Time (h)	bp (°C, mmHg)	Yield (%)
PA	<i>n</i> -Propanol (1)	Acrylic acid (1.1)	MC (150 mL)	<i>p</i> -TsOH (19.0)	45–50	5	56, 54	34
NPA	2-Nitropropanol (0.5)	Acrylic acid (0.55)	Benzene (100 mL)	<i>p</i> -TsOH (9.5)	75–80	6	93, 10	56
DNPA	2,2-Dinitropropanol (0.5)	Acrylic acid (0.55)	EDC (150 mL)	PPA (150)	70	18	108, 8	66
PMA	<i>n</i> -Propanol (0.5)	Methacrylic acid (0.55)	Benzene (100 mL)	<i>p</i> -TsOH (9.5)	75–80	4	70, 65	70
NPMA	2-Nitropropanol (0.5)	Methacrylic acid (0.55)	Benzene (100 mL)	<i>p</i> -TsOH (9.5)	75–80	6	106, 12	38
DNPMA	2,2-Dinitropropanol (0.5)	Methacrylic acid (0.55)	EDC (150 mL)	PPA (150)	70	18	123, 12	74

MC, methylene chloride; EDC, ethylene chloride; PPA, poly(phosphoric acid); *p*-TsOH, *p*-toluenesulfonic acid.

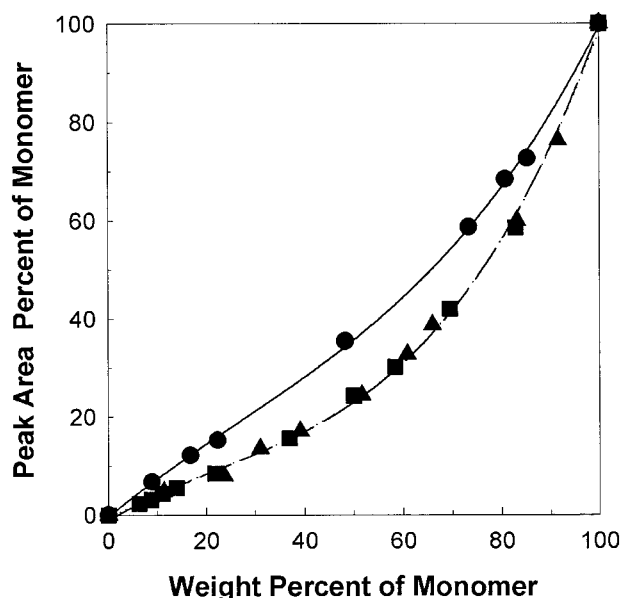


Figure 1 The calibration curve of weight percent vs. peak area percent for monomer and tetraline: ● PA, ■ NPA, ▲ DNPA.

(0.1 mol) of polymeric phosphoric acid, 2 g (0.018 mol) of hydroquinone, and 150 mL of ethylene dichloride in a 1-L round flask with condenser was refluxed overnight. After the reaction was completed, the upper ethylene dichloride layer was decanted, and the down layer was washed with ethylene dichloride several times. The ethylene dichloride solution gathered was washed with dilute NaOH aqueous solution and saturated NaCl aqueous solution and distilled water several times and dried with magnesium sulfate. DNPA was distilled at 108°C in 8 mmHg, yielding 66.3 g (65%) with greater than 98% of purity. For other monomers, such as *n*-propyl acrylate (PA), 2-nitropropyl acrylate (NPA), *n*-propyl methacrylate (PMA), 2-nitropropyl methacrylate (NPMA), and 2,2-dinitropropyl methacrylate (DNPMA), the preparation was carried out under various conditions. The results are shown in Table I.

Determination of Heat of Polymerization

Calorimetry

Dynamic as well as isothermal calorimetric measurements were performed using the Mettler/Toledo DSC model 821 calibrated for temperature and enthalpy response with indium. The enthalpies were measured with an accuracy of within 1% reproducibility. Dynamic and isothermal polymerization were carried out by placing the medium-pressure stainless pans containing the

monomer or mixture (monomer–initiator) into a DSC cell. In dynamic polymerization, the scanning rate was 3°C/min.

Gas Chromatography

Using Hewlett Packard GC model 5880, the peak area ratio of monomer and tetraline as a standard material were measured as a function of weight ratio of those to compose the calibration curves (Fig. 1). Immediately after each DSC run, the contents of pans were dissolved in tetrahydrofuran (THF) to determine the conversion ratio by GC.

RESULTS AND DISCUSSION

The possibility of free radical self-initiated bulk polymerization of each monomer was investigated under isothermal condition in the range of 110–150°C for 4 h. Only PA and PMA monomers were easily polymerized without an initiator under an experimental condition used in this study. This behavior was in agreement with the fact that polymerization of these monomers occurred even with a high content of the inhibitor during the esterification and vacuum distillation in the preparation of the monomer. Other monomers did not self-polymerize at temperatures below 150°C. And the oxidation by nitro group and polymeriza-

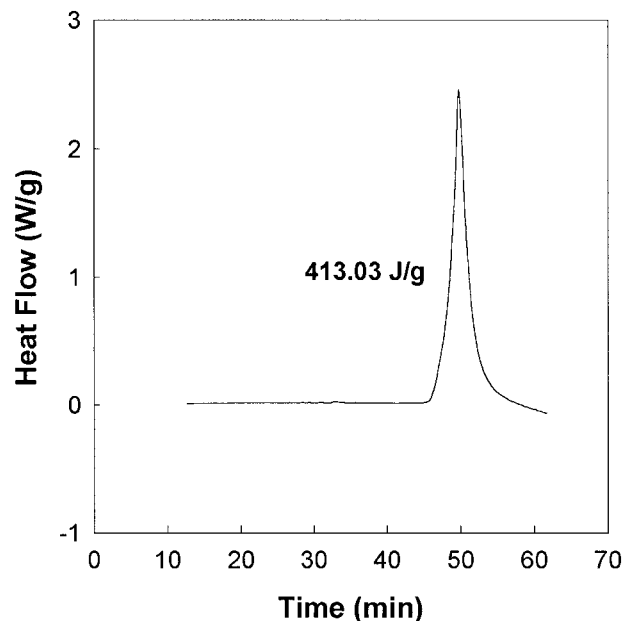


Figure 2 Isothermal DSC thermogram for pure PA at 130°C.

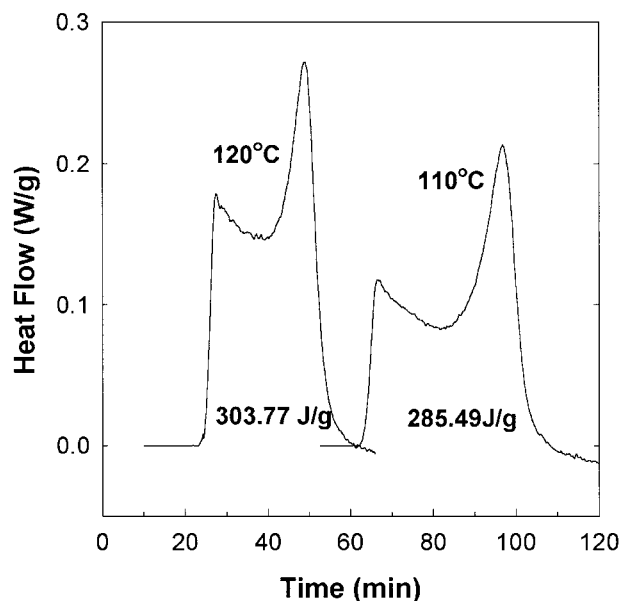


Figure 3 Isothermal DSC thermogram for pure PMA.

tion occurred simultaneously above 150°C, which made it difficult to distinguish the heat of polymerization from the exothermic phenomenon. Figure 2 shows a typical isothermal trace at 130°C of PA. It is evident from Figure 3 that the polymerization rates become faster, with higher temperatures. Two abnormal peaks on each isothermal curve of PMA in Figure 3 is thought to have a relation with the gel effect and polymer-

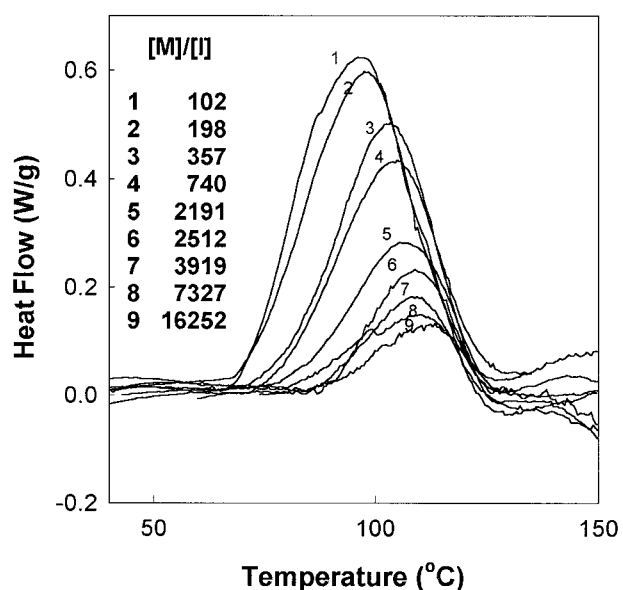


Figure 4 Change in DSC thermogram with molar ratio of [DNPA]/[AIBN].

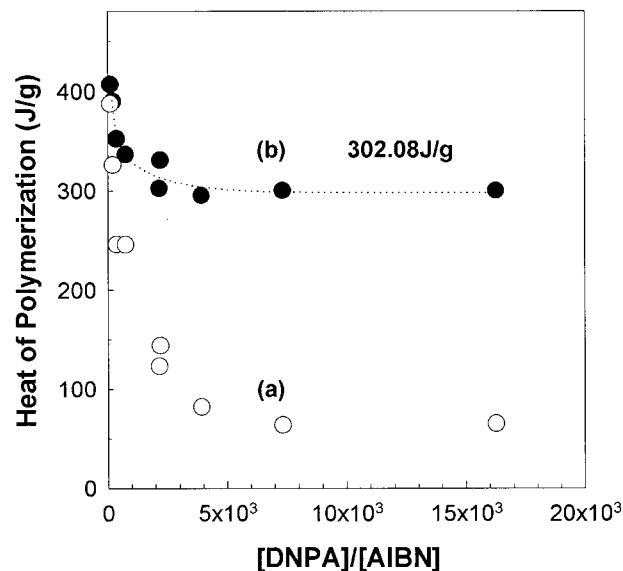


Figure 5 Change in the heat of polymerization with molar ratio of [DNPA]/[AIBN]. (a) apparent ΔH , (b) corrected ΔH .

ization rate, as there was no change in sample weight during each run, and the polymer was detected by GPC after each run. After correcting for incomplete conversion of monomer, the values of ΔH_p for PA and PMA were found to be 73.21 and 56.07 kJ/mol, respectively. And ΔH_p for PMA obtained in the present work agrees well with the value reported earlier.¹²

Propyl(meth)acrylate monomers containing nitro groups can be easily polymerized by free-radical initiator such as 2,2'-azobisisobutyronitrile (AIBN). In an isothermal polymerization with a mixture (i.e., monomer–initiator), some monomers started to polymerize in settling time and therefore the heat of polymerization could not be calculated accurately. Dynamic test was useful to avoid the premature exhaustion of initiator.

Table II Initiator Concentration and Apparent Heat and Conversion and Corrected Heat of PA Polymerization

[M]/[I]	H_{app} (J/g)	Conversion	H_{corr} (J/g)
214	586.54	0.919	716.54
418	546.33	0.775	705.11
1397	522.00	0.762	685.12
2295	433.39	0.640	677.26
11810	382.02	0.802	646.67
22554	518.37	0.590	643.25
46651	193.98	0.302	647.24

Table III Initiator Concentration and Apparent Heat and Conversion and Corrected Heat of NPA Polymerization

[M]/[I]	H_{app} (J/g)	Conversion	H_{corr} (J/g)
156	515.35	0.715	675.37
333	400.93	0.617	629.16
785	221.09	0.440	492.22
1848	171.54	0.367	462.85
3624	90.83	0.212	426.14
8292	45.50	0.110	412.05
16178	49.35	0.128	385.15
33379	27.28	0.073	375.67
72487	21.35	0.057	376.42

In DNPA as well as other monomers, exothermic peaks showed a remarkable dependency on the amount of the AIBN as seen in Figure 4. The peak area on the DSC curve decreased with the decrease in the amount of initiator and the onset temperature is contrary. The plot of ΔH_p vs. [M]/[I] shows the exponential decay curve. The values of ΔH_p shown in Figure 5(a) were obtained directly from DSC. When the ΔH_p , obtained after correcting for both the decomposition heat of AIBN and for incomplete conversion of monomer to polymer, were plotted against molar ratio, a constant value of ΔH_p (61.62 kJ/mol) was obtained in the low concentration range of AIBN in Figure 5(b). And the phenomenon that values of ΔH_p within the high concentration range of AIBN obtained are higher than the constant value may be attributable to the chain transfer reaction of the initiator, as discussed by Mahato et al.⁶ If it is reasonable to assume that the contribution of the chain transfer reaction is negligibly small in the low concentration range of AIBN, the constant

Table IV Initiator Concentration and Apparent Heat and Conversion and Corrected Heat of DNPA Polymerization

[M]/[I]	H_{app} (J/g)	Conversion	H_{corr} (J/g)
102	387.59	0.826	414.51
198	326.33	0.777	396.20
357	246.37	0.656	358.65
740	245.98	0.709	338.69
2191	144.02	0.427	334.08
2152	123.18	0.399	306.07
3919	82.14	0.273	298.79
7327	63.72	0.210	303.01
16259	65.10	0.216	301.55

Table V Initiator Concentration and Apparent Heat and Conversion and Corrected Heat of PMA Polymerization

[M]/[I]	H_{app} (J/g)	Conversion	H_{corr} (J/g)
201	418.59	0.803	475.27
459	454.04	0.882	494.14
1271	331.21	0.646	505.14
2206	458.82	0.953	478.39
4510	465.79	0.939	493.87
12306	355.35	0.769	461.33
18517	300.72	0.683	440.17
41152	197.41	0.446	442.79

value of ΔH_p may be considered the ΔH_p of DNPA. The full experimental details of more than 50 polymerization runs on each monomers studied are given in Tables II–VII. The results are summarized in Table VIII. It was found that the ΔH_p values obtained from both the dynamic test and the isothermal test were not distinguished from each other, as shown in Table VIII.

The attachment of one nitro group on the C6 atom of NPA results in the surprisingly low value of ΔH_p (59.82 kJ/mol). But the markedly change in ΔH_p is not shown although the attachment number of nitro group increases from one to two. This phenomenon of nitropropyl acrylates is similar to that of nitropropyl methacrylates.

To find the reason, the conformations of monomers have been investigated with the PM3 Hamiltonian¹³ in a MOPAC program.¹⁴ Each monomer has five rotatable bonds, which cause to generate numerous conformations. Thus, performing all the conformational energy surfaces will take so much efforts by rotating five different bonds simultaneously, even with a reasonably crude interval in dihedral angles. Rather doing this, we

Table VI Initiator Concentration and Apparent Heat and Conversion and Corrected Heat of NPMA Polymerization

[M]/[I]	H_{app} (J/g)	Conversion	H_{corr} (J/g)
125	275.79	0.703	335.93
274	236.39	0.692	314.32
1472	183.62	0.571	316.27
2972	83.21	0.270	306.06
4315	68.36	0.231	293.65
5127	31.60	0.107	293.61
7527	31.28	0.109	286.87
17510	20.10	0.071	284.32

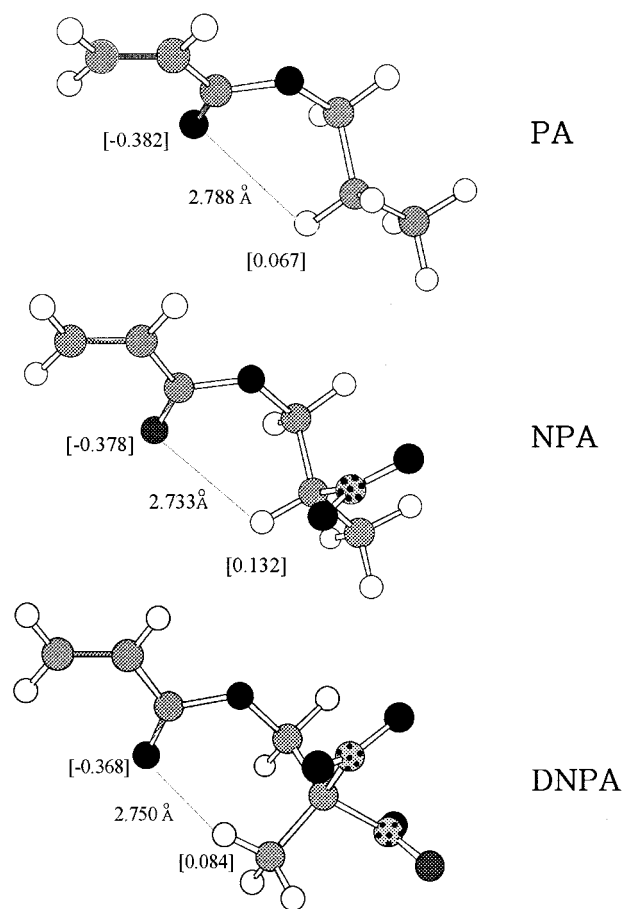
Table VII Initiator Concentration and Apparent Heat and Conversion and Corrected Heat of DNPMA Polymerization

[M]/[I]	H_{app} (J/g)	Conversion	H_{corr} (J/g)
82	272.49	0.870	247.38
162	242.45	0.857	255.95
661	171.84	0.703	235.68
423	191.03	0.760	238.13
951	144.30	0.613	227.87
1815	112.75	0.536	207.18
4345	59.99	0.292	203.99
9161	18.28	0.087	207.21

have used the stable conformational fragments by ignoring the secondary interactions, whose effects are relatively small. The conformational stability of each conformational fragment are confirmed with a dihedral angle driver calculation for each torsional bond. We have found that the double bonds in the monomers studied in this work are stable in two conformations—eclipsed and anti—with the single bonds remaining stable at three different staggered alignments.

Bearing these results in mind, we have investigated the most stable conformation in each monomer by hooking these stable torsional angles up to assemble starting geometries. We have generated a total of 36 conformers for each monomer. The number of calculated conformers are reduced in PA, DNPA, PMA, and DNPMA, which have a mirror image. After calculating all the possible conformations of these monomers, we have compared the heats of formation from the PM3 method, and obtained the most stable conformations, in which the monomers are supposed to be present. The most stable conformations in all the monomers utilized in this study have depicted in Figures 6 and 7.

In a series of acrylate monomers, the most stable conformations bear a hydrogen bond between the O(=C) atom and the H atom attached to either C6 or C7 atoms. In PA and NPA where the H atom is available at the C6 position, the

**Figure 6** The most stable conformer of PA, NPA and DNPA.

conformation is most stable by forming a hydrogen bond between the C=O and H-C6 bond. On the other hand, in DNPA where the H atoms is not available at the C6 position, the most stable conformation still has a hydrogen bond by utilizing the H atom at the C7 position. Although it is hard to quantify the exact conformational stabilities in the monomers through the hydrogen bond, the strengths of hydrogen bonds are often gauged by the distance between the donor and the acceptor.¹⁵ Based on the distance between the donor and the acceptor, NPA appears to have a strongest hydrogen bond, compared with PA and

Table VIII Heat of Polymerization of Monomers Obtained from Dynamic DSC Analysis

	PA	NPA	DNPA	PMA	NPMA	DNPMA
H_p (kJ/mol)	73.21 ^a 73.51	59.82	61.62	56.07 ^a 56.51	49.27	45.15

^a Isothermal DSC analysis.

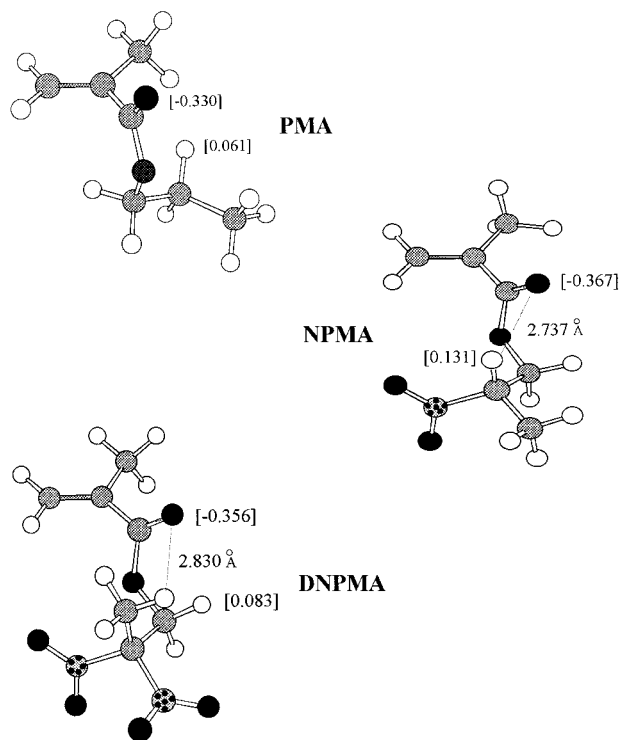


Figure 7 The most stable conformers of PMA, NPMA and DNPA.

DNPA. The distance between the O(=C2) atom and the H(-C6) atom in NPA is calculated to be 2.733 Å, whereas those in PA and DNPA are computed to be 2.788 Å, and 2.750 Å, respectively. In addition, we also investigated the excess charges of some atoms relevant to these hydrogen bonds. Interestingly, the positive charge of the H(-C6) atom that forms a hydrogen bond in NPA is significantly larger than those of corresponding atoms in PA and DNPA. This charge analysis appears to support the strength of hydrogen bonds in this series of acrylate monomers.

In a series of methacrylate monomers, the C=O bond becomes eclipsed with the C=C bond due to the presence of the Me group at the C2 position. In this alignment, we believe that the conjugation between double bonds will be lost, but the stability due to the conjugation between double bonds is relatively small using the PM3 method. The stability due to the conjugation between these bonds is estimated to be only 1–2 kcal/mol, when it is computed by using the model compounds and some conformations from acrylate monomers. In this series of monomers, the trend in the strength of hydrogen bond is similar

to the acrylate monomers due to the successive attachment of nitro groups. As is well known,¹⁶ the hydrogen bond that stabilizes monomers is not as important in the polymer because its steric constraints prevent the required lining up of substituents. Thus, the hydrogen bond decreases the heat of polymerization.

Conclusively, a contributing main factor to the lowering of ΔH_p for NPA and NPMA is the hydrogen bond between the O(=C) and the H atom attached at the C6 position. In the cases of DNPA and DNPMA, the weak hydrogen bond and steric hindrance are considered to play a role of the lowering of ΔH_p . And also, the ΔH_p value for methacrylates is lowered relative to that for acrylates due to increased steric hindrance in polymer, although the acrylate monomers are more stable than the methacrylate monomers.

REFERENCES

- Joshi, R. M. *Makromol Chem* 1962, 55, 32.
- Severini, F.; Gallo, R.; Ricca, G. *Thermochim Acta* 1988, 132, 161.
- Gallo, R.; Severini, F. *Thermochim Acta* 1989, 147, 93.
- Alberda van Eenstein, G. O. R.; Tan, Y. Y. *Eur Polym J* 1981, 17, 839.
- Kamite, I. A.; Palomares, F.; Cesteros, L. C.; Laborra, C.; Dominguez, E. *Thermochim Acta* 1989, 142, 317.
- Mahato, P. K.; Chanda, D.; Borthakur, A.; Rao, K. V. *Thermochim Acta* 1993, 222, 265.
- Tanaka, A.; Sasaki, K.; Hozumi, Y.; Hashimoto, O. *J Appl Polym Sci* 1964, 8, 1787.
- Takahashi, K.; Abe, S.; Namba, K. *J Appl Polym Sci* 1968, 12, 1683.
- Kaplan, R. B.; Shechter, H. *J Am Chem Soc* 1961, 83, 3536.
- Hamel, E. E.; Dehn, J.; Love, J. A.; Scigliano, J. J.; Swift, A. A. *IEC Product Res Dev* 1962, 1, 108.
- Kim, C. S. *Synthesis of Hydroxy-Terminated Polymer and Improved Characterization of Hydroxy-Terminated Prepolymers*; AD report AD A127469 (AFRPAK-TR-83-002), 1983.
- Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; John Wiley & Sons: New York, 1975.
- Stewart, J. J. P. *J Comput Chem* 1989, 10, 209.
- Stewart, J. J. P. *MOPAC 6.0*, QCPE No. 455.
- Smith, D. A., Ed., *Modeling the Hydrogen Bond*; American Chemical Society: Washington, DC, 1994.
- Ordian, G. *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, 1991.