

## Polymer-Diluent Interactions of Some Nitrocellulose-Nitrate Ester Systems

R. L. BROOKS and A. R. LAWRENCE, *Research and Development  
Department, U. S. Naval Propellant Plant, Indian Head, Maryland*

### Synopsis

The Flory-Huggins interaction  $\chi$  and the closely related heat of mixing parameter  $B$  were determined for several nitrocellulose-nitrate ester systems. A micromethod which permitted the use of a simplified version of the Flory equation was successful in evaluating the effects of two series of nitrate ester diluents with nitrocellulose. A distinct difference exists between the effect of  $\alpha,\omega$ - and  $\alpha,\beta$ -substituted diluents as shown by the  $\chi$  and  $B$  parameters. Generally, the terminally substituted nitrate esters appear to be the better solvents.

### INTRODUCTION

Much interest has been generated in the development of methods for determining types and degrees of polymer-diluent interactions. We have used a micromethod developed by Anagnostopoulos<sup>1</sup> to determine the Flory-Huggins interaction parameter  $\chi$  and the closely related heat of mixing parameter  $B$  for several nitrocellulose-nitrate ester systems. The method appears to be particularly useful in instances where the melting point of a polymer is difficult to detect even though crystallinity has been established by x-ray diffraction techniques. In this instance, the size of the polymer particles (1-10  $\mu$ ) also presented a unique problem.

Because of our interest in diluents and their relationship with polymers, especially those diluents which are also plasticizers, this method presented a unique way to study the effect of molecular structure on polymer-diluent interactions.

The method is based on Flory's<sup>2,3</sup> thermodynamic treatment which shows that the equilibrium melting temperature of a crystalline polymer may be depressed by a monomeric diluent incorporated in the polymer. The magnitude of the depression depends on the nature of the polymer, the concentration of the diluent, and the degree of the polymer-diluent interaction.

The depressed melting point  $T_m$  of a polymer when mixed with a diluent is a function of the volume fraction of the diluent  $v_1$  and the parameter  $\chi$ :

$$1/T_m = 1/T_m^\circ + (R/\Delta H_u)(V_u/V_1)(v_1 - \chi v_1^2) \quad (1)$$

where  $T_m^\circ$  is the melting point of the pure polymer,  $R$  is the gas constant,  $\Delta H_u$  is the heat of fusion per mole of repeating polymer unit,  $V_1$  is the

molar volume of diluent at  $T_m$ ,  $V_u$  is the molar volume of polymer repeating unit,  $v_1$  is the volume fraction of diluent  $\chi$ , the Flory-Huggins parameter. This treatment has been applied in a number of cases<sup>4-7</sup> where, due to crystallinity of the polymer, the melting temperature could be determined by conventional methods of dilatometry or visual detection. The parameter  $\chi^{2,3}$  is defined by

$$\chi = BV_1/RT \quad (2)$$

$\chi$  and  $B$  were determined on the basis of a microscopically observed characteristic change and the temperature at which this change occurred. This was called the depressed melting point and identified with  $T_m$  in eq. (1). It is pointed out that the high degree of dilution permitted the approximation  $v_1 = 1.0$ ,<sup>1</sup> which allows simplification of eq. (1) which becomes

$$1/T_m = 1/T_m^\circ + (R/\Delta H_u)(V_u/V_1)(1 - \chi) \quad (3)$$

This approximation compresses the value of  $\chi$  to an upper limit of unity and this distorts the higher values of  $\chi$ , but does not lessen the value as a relative measurement of polymer-diluent interactions.

## EXPERIMENTAL

### Materials

The nitrocellulose used contained 12.16% nitrogen and had a particle size in the range of 1-10  $\mu$ . All nitrated esters were prepared by nitrating the corresponding diol with a 1:1 mixture of sulfuric and nitric acids.

TABLE I  
Characterization of Polymer Diluents

Diluent	$T_m$ , °C.	$V_1$	$\chi$	$B$ , cal./cc.
1,2-Dinitroxyethane	24	83	-0.39	-2.77
1,3-Dinitroxypropane	36	111	-0.33	-1.84
1,4-Dinitroxybutane	43	139	-0.27	-1.23
1,5-Dinitroxy pentane	53	155	-0.15	-0.63
1,6-Dinitroxyhexane	61	172	-0.11	-0.52
1,7-Dinitroxyheptane	77	189	-0.07	-0.26
1,8-Dinitroxyoctane	85	233	-0.036	-0.10
1,9-Dinitroxy nonane	97	329	-0.027	-0.06
1,10-Dinitroxydecane	111	660	-0.009	-0.01
1,2-Dinitroxypropane	56	119	+0.128	0.70
1,2-Dinitroxybutane	80	139	+0.256	1.29
1,2-Dinitroxy pentane	107	172	+0.345	1.51
1,2-Dinitroxyhexane	130	198	+0.378	1.53
1,2-Dinitroxyheptane	160	198	+0.436	1.69
1,2-Dinitroxyoctane	178	246	+0.438	1.60
<i>trans</i> 1,2-Dinitroxy cyclopentane	75	151.18	+0.232	1.06
<i>cis</i> 1,2-Dinitroxy cyclopentane	88	163.07	+0.298	1.31

### Equipment

The conventional microscope, equipped with a micro hot stage and a Bausch and Lomb camera for making photomicrographs was used.

### Procedures

In a typical experiment, a few particles of the polymer were put on a slide, mixed with a drop of diluent, and positioned on the hot stage. Exposures (Fig. 1) were made at intervals to show the progressive change of the particles upon heating. An advantage of this method was that photographic recordings aided in reproducing the depressed melting point determinations. A heating rate of  $0.5^{\circ}\text{C./min.}$  was used to give reproducible endpoints to within  $\pm 2^{\circ}\text{C.}$  The temperature was raised until the swollen particle lost its outline. This was taken as the apparent melting point  $T_m$ .

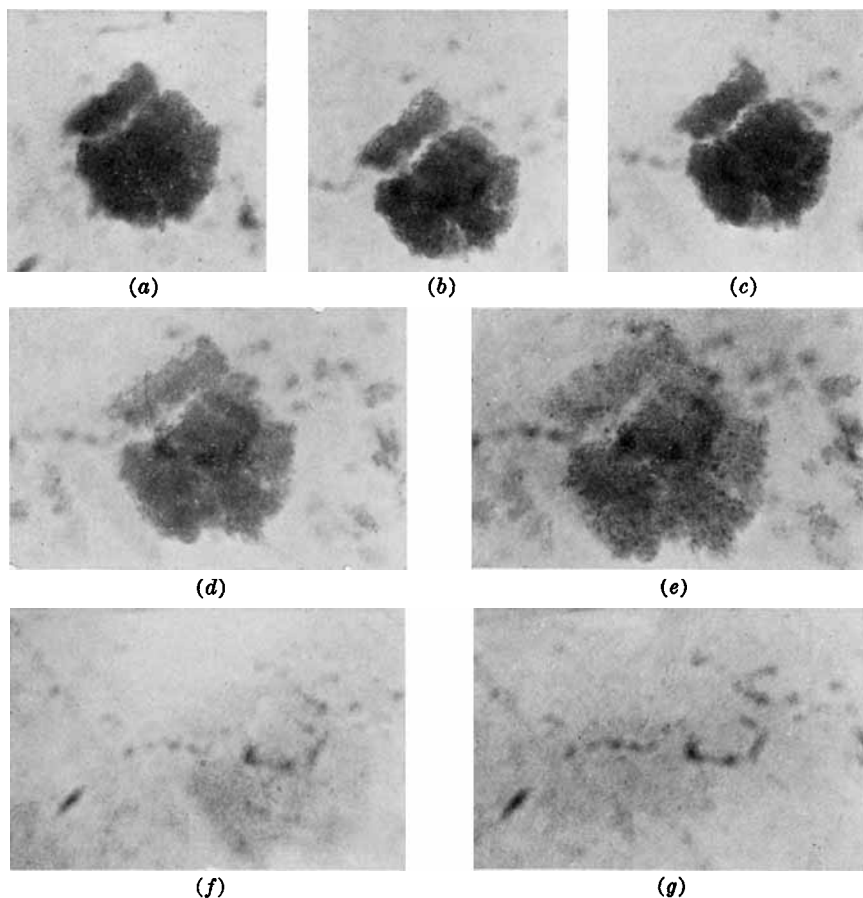


Fig. 1. Progressive changes in the polymer-diluent composition with increasing temperature: (a)  $22.5^{\circ}\text{C.}$ ; (b)  $26.5^{\circ}\text{C.}$ ; (c)  $50^{\circ}\text{C.}$ ; (d)  $55^{\circ}\text{C.}$ ; (e)  $56^{\circ}\text{C.}$ ; (f)  $58^{\circ}\text{C.}$ ; (g)  $60\text{--}61^{\circ}\text{C.}$  Magnification  $200\times$ .

## RESULTS

The values of  $\chi$  and  $B$  for the two homologous series of nitrated esters are listed in Table I, along with the apparent melting points. The molar volume of diluent was calculated from molecular weight of diluent and the estimated density of the diluent at the gel-to-sol transformation temperature. The melting point of the pure polymer, the heat of fusion (1350 cal.), and the molar volume of polymer, (repeating unit 165) were taken from the literature.<sup>7,8</sup>

## DISCUSSION

The differences in the solvent qualities of the two homologous series are quite apparent from Figures 2 and 3. If  $\chi$  and  $B$  are significant for evalu-

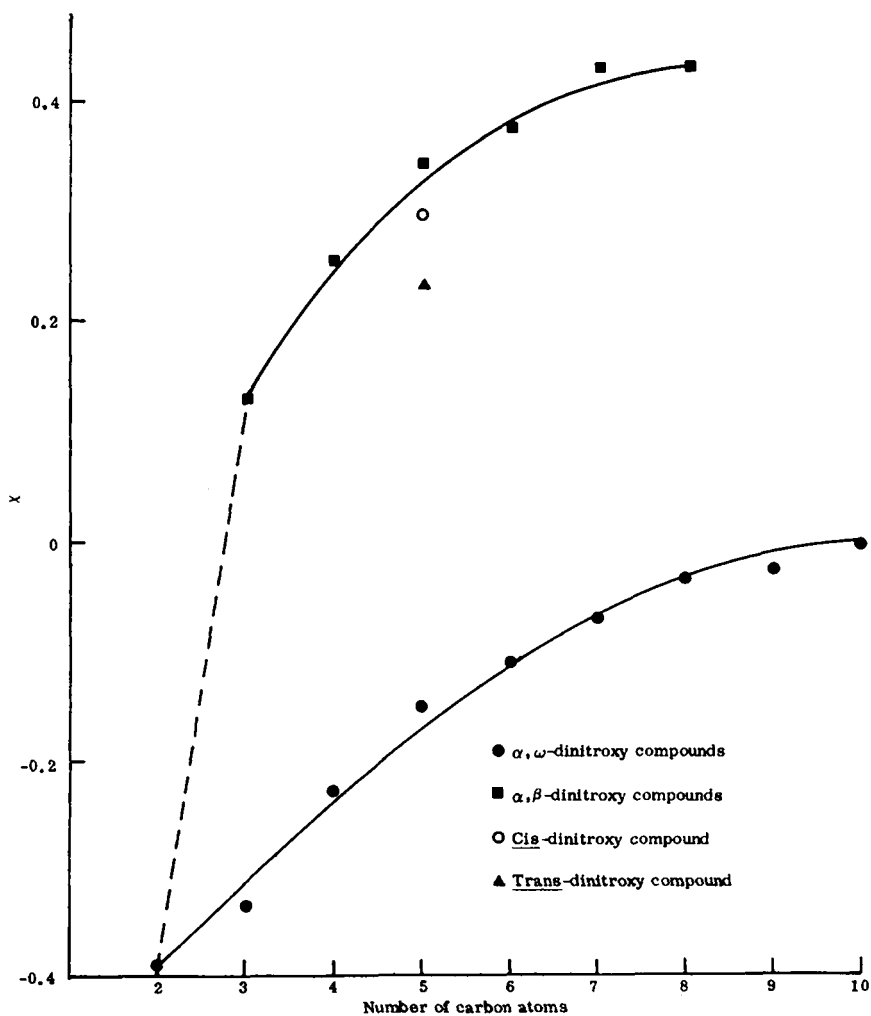


Figure 2.

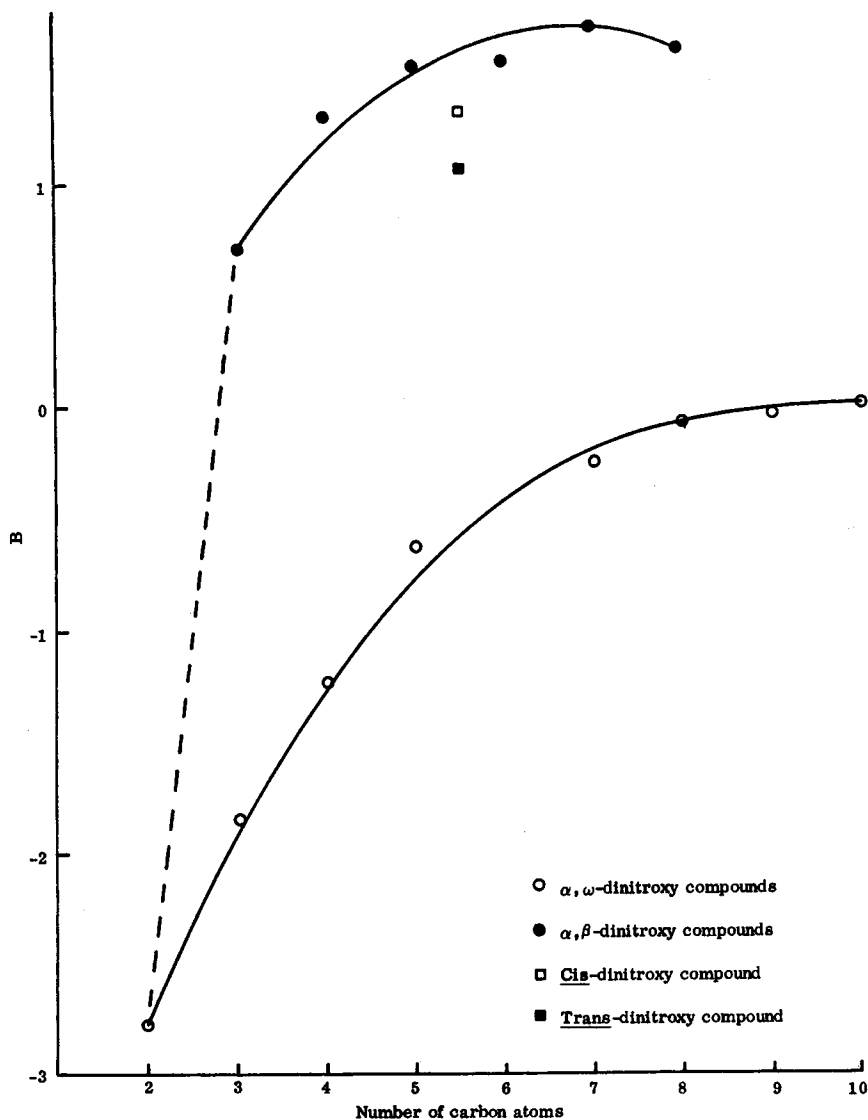


Figure 3.

ating diluents, then clearly the  $\alpha, \omega$  series of diluents is superior to the  $\alpha, \beta$  series. There is the interesting observation however, that these results differ from Anagnostopoulos,<sup>9</sup> evaluation of a series of phthalate esters. Here he found that within a given ester series, the parameter  $B$  decreases with increasing chain length, reaching a minimum and then increasing as the side chain assumes still greater lengths.

Moreover, the fact that the  $\alpha, \omega$  series appear to be the better diluents may point out the effect of terminally substituted polar groups over against neighboring polar groups. If indeed, typical models of each series are

examined, one reasons that the  $\alpha,\omega$  series have nitroxy groups that are rather free to rotate around carbon-carbon bonds while in the  $\alpha,\beta$  series, rotation around the carbon-carbon bond is somewhat restricted.

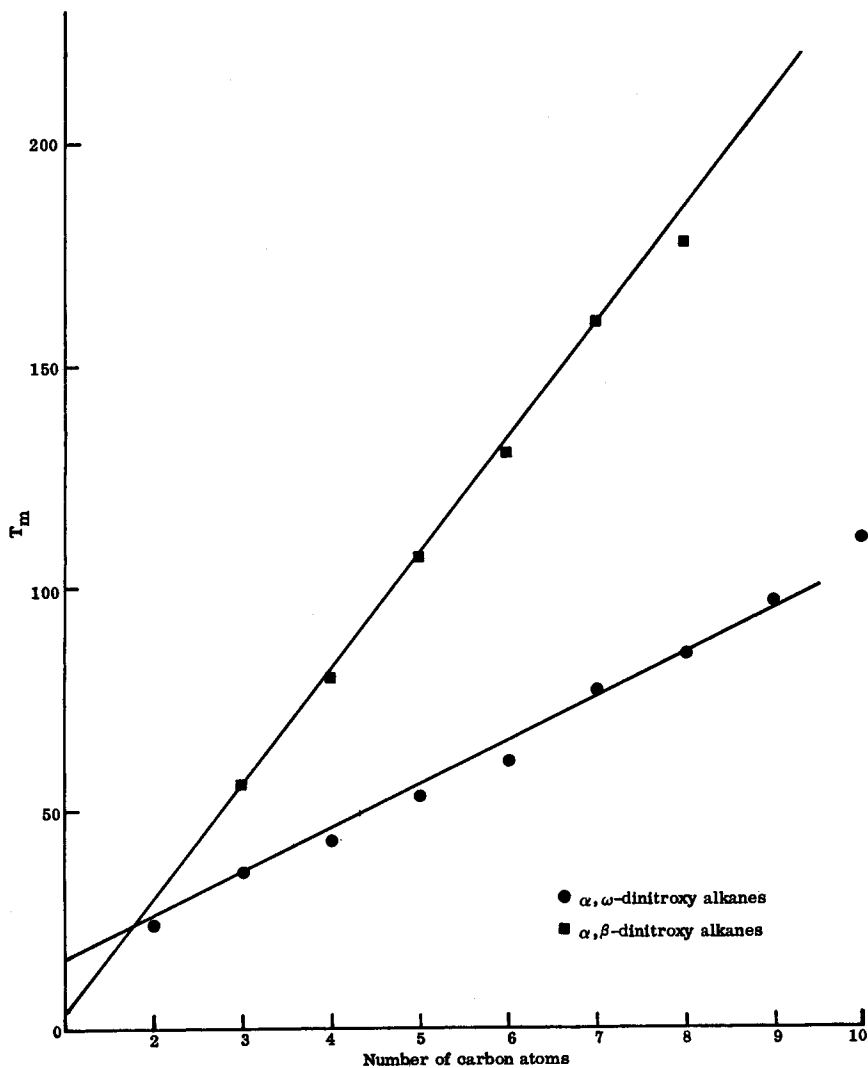


Figure 4.

It is possible that this restricted rotation might be indicated by the fact that higher temperatures are required to reach  $T_m$  or the gel-to-sol state for the same isomers (Fig. 4).

It appears then, that a particular *cis* or *trans* configuration was being achieved with chain length. The  $\chi$  measurements indicated also that the configuration change might be more prominent in the  $\alpha,\omega$  series. Thus one

might assume that the diluents having the dinitroxy groups in the preferred configuration would display the better solvent properties.

To test this hypothesis, the  $\chi$  and  $B$  values of the *cis*- and *trans*-dinitroxy cyclopentanes were also measured, the reason being that these isomers apparently do not readily interconvert to one another. One would expect the *trans* compound to be the better diluent and it is, according to the  $\chi$  and  $B$  values (Table I).

### CONCLUSIONS

$\chi$  and  $B$  values were found to increase with molecular size, indicating that the smaller dinitroxy molecules of both series are the better diluents. These measurements may also indicate how stereoelectivity might be used to obtain the desired solvent quality even within the same series.

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### Résumé

Le paramètre d'interaction  $\chi$  de Flory-Huggins et le paramètre  $B$  de la chaleur de mélange qui lui est relié étroitement, ont été déterminés pour plusieurs systèmes nitrocellulose-esters nitriques. Une microméthode qui permet l'emploi d'une version simplifiée de l'équation de Flory, a été employée avec succès pour évaluer les effets de deux séries de diluants de l'ester nitrique avec la nitrocellulose. Une différence marquée existe entre l'effet de diluants  $\alpha,\omega$  et  $\alpha,\beta$  substitués, comme le prouvent les paramètres  $\chi$  et  $B$ . En général les esters nitriques, substitués à leurs extrémités, apparaissent comme étant de meilleurs solvants.

### Zusammenfassung

Der Flory-Huggins'sche Wechselwirkungsparameter  $\chi$  und der damit eng verbundene Parameter der Mischungswärme  $B$  wurden für mehrere Nitrozellulosenitratestersysteme bestimmt. Eine Mikromethode, die die Verwendung einer vereinfachten Form der Flory-Gleichung erlaubt, wurde erfolgreich zur Berechnung der Einflüsse von zwei Reihen von Nitratesterlösungsmitteln auf Nitrozellulose angewendet. Wie die  $\chi$ - und  $B$ -Parameter zeigen, besteht ein deutlicher Unterschied zwischen den Einflüssen von  $\alpha,\omega$ - und  $\alpha,\beta$ -substituierten Verdünnungsmitteln. Im allgemeinen scheinen die endständigsubstituierten Nitrate die besseren Lösungsmittel zu sein.

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