*Mendeleev Commun.*, 1998, 8(4), 159–160

# Low-temperature radiation polymerization of cyanogen bromide

**Galina A. Kichigina,* Pavel S. Mozhaev, Dmitriy P. Kiryukhin and Igor M. Barkalov**

*Institute for Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 515 3588*

**The absence in crystalline cyanogen bromide of intermolecular chains with strong N···H hydrogen bonds typical of the HCN crystal causes a difference in cryopolymerization in these monomers. Heat release is observed during defrosting of radiolysed cyanogen bromide, connected with its polymerization at 220–230 K. There is another heat release due to polymerization of cyanogen bromide in the melting region. The dependence of the yield of the polymer forming in the melting regions on the irradiation dose has an extreme character. We assume that the suppression of the polymerization of cyanogen bromide in the melting region is connected with progressive destruction of the matrix structure during irradiation.**

Radiation-induced cryochemical conversion of solid hydrogen cyanide, its polymerization and copolymerization are described in refs. 1–3. Hydrogen cyanide is converted into a polymer more effectively in its copolymerization with acetaldehyde and ethylene oxide.[4,5] Radiolysis of solid HCN at 77 K leads to stabilization of the active centres of the radical and its ionic nature (for more details see refs. 6–9). Further heating of the system in the solid phase leads to formation of a conjugate polymer of the $-[\mathrm{HC{=}N}]_n-$ type [8,9] and tetramer crystals (1,2-diaminomaleinodinitrile).[3] The forming polymer gives a singlet EPR spectrum typical of polyconjugate systems, its molecular mass being $M = 1540\pm50$.[7,9]

According to the literature,[10] the tetragonal crystal structure of HCN possesses intermolecular chains bound by strong N···H hydrogen bonds of the 'head-to-tail' type, which leads to a weakening of the C···N interactions. In this connection it is assumed that the most probable reaction during radiolysis of HCN crystals is elimination of a proton and formation of a complex with a neighbouring molecule, $[\mathrm{HCN\cdots H}]^+$. An electron settling on this complex results in the formation of a $\mathrm{H_2C{=}N\cdot}$ radical. We thus assume that the main intermediate particle that is stabilized during low-temperature radiolysis of the HCN crystal is a complex cation of the $[\mathrm{HCN\cdots H}]^+$ type.[6] This probably determines the main direction for all subsequent cryochemical conversions. Since there are no hydrogen bonds in cyanogen bromide, it would be of interest to compare the tendency to cryopolymerization of this compound and hydrogen cyanide.

The aim of the present work is to investigate the low-temperature radiation-induced polymerization of cyanogen bromide.[†]

Radiolysis of crystalline cyanogen bromide at 77 K leads to an accumulation of stabilized active centres in it. The radiation yield of these centres, determined from the initial section of the accumulation curve, is $G = 7.8$ which almost coincides with the radiation yield for the accumulation of paramagnetic centres in hydrogen cyanide under the same conditions.[8]

The calorimetric curve for cyanogen bromide heating from 80 K shows only an endothermic peak due to the monomer crystals melting at 324 K (Figure 1, curve *1*). The melting heat is $H = 11.6$ kJ mol$^{-1}$. A small heat release peak is observed during defrosting of radiolysed cyanogen bromide, which is connected with its polymerization in the temperature range 220–230 K. In the course of further heating in the premelting and melting regions, the calorimeter also shows heat release due to polymerization of cyanogen bromide (Figure 1, curve *2*). Such a picture emerges only for doses of preirradiation ≤ 1 MGy. At larger doses heat release is observed only in the range 220–230 K, while the heat release in the premelting region is lost.

After defrosting, the unreacted cyanogen bromide is removed *in vacuo*, and the polymer yield is determined gravimetrically. A series of calorimetric measurements of the sort given in Figure 1 and gravimetric measurements of the polymer yield after defrosting give a mean specific heat for polymerization of cyanogen bromide, $H = 86\pm2$ kJ mol$^{-1}$. This value is close to that for the cryopolymerization of hydrogen cyanide, $H = 85$ kJ mol$^{-1}$.[5] The isolated polymer is orange–red in colour, which is typical of conjugated systems. The polymer is unstable and decomposes during storage at room temperature. The IR spectrum of the cyanogen bromide polymer, as distinct from the IR absorption spectra of the initial monomer, has no absorption band $\nu_s$ C≡N at 2180 cm$^{-1}$, while a band due to the C=N bond vibration appears at 1700 cm$^{-1}$.

The dependence of the polymer yield on the preirradiation dose is given in Figure 2. It has an unusually extreme view. In the dose range 0–980 kGy, the polymer yield increases monotonously reaching a maximum value of ~9% at 980 kGy. The polymer yield of hydrogen cyanide under the same conditions is considerably lower, ~2.5% at a dose of 800 kGy.[1] Further increase of the dose leads to a yield reduction down to ~4% at 1.2 MGy, which remains practically unchanged up to a dose of 2 MGy (Figure 2). Assuming that all the isolated

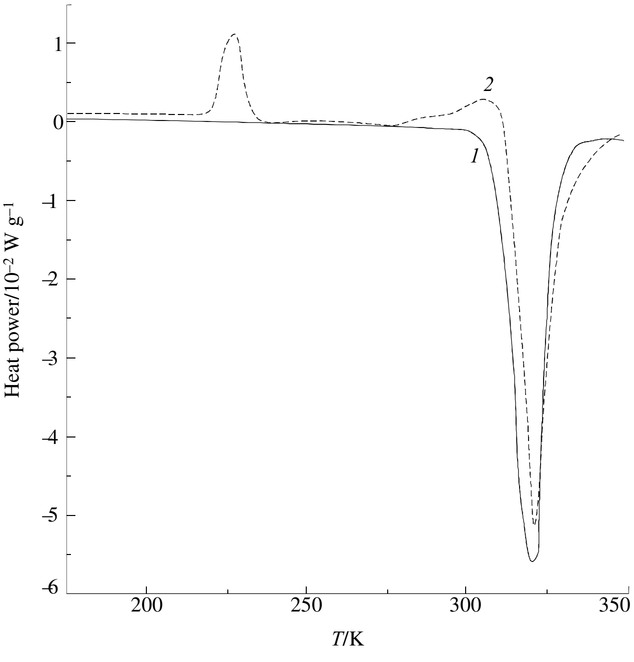

**Figure 1** Calorimetric heating curves for cyanogen bromide: (*1*) unirradiated and (*2*) -irradiated at 77 K with a dose of 980 kGy.

---

[†] *Experimental details.* The preparation and purification of cyanogen bromide has been described.[11] Its major characteristics are as follows: mp 50–51 °C, bp 61 °C. The phase state of the system and the kinetics of cryopolymerization were studied by a calorimetric technique.[12] Radiolysis of the samples examined was performed in a vacuum in calorimetric sealed ampoules at 77 K using a 'Gamma-tok' set-up with $^{60}$Co -rays, dose rate 1.4 Gy s$^{-1}$. The dose rate was measured by an ionisation chamber and the ferrosulfate method. The EPR spectra of the free radicals were recorded on an EPR-21 radiospectrometer at 77 K. IR absorption spectra in the range 400–3600 cm$^{-1}$ were recorded on a UR-20 spectrometer. The IR samples were prepared as KBr pellets.

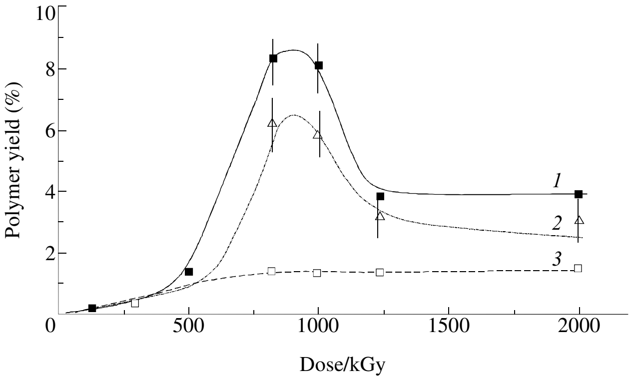

**Figure 2** Dependence of the polymer yield on the preirradiation dose at 77 K: (*1*) integral, (*2*) in the temperature region of premelting and melting for cyanogen bromide and (*3*) in the temperature region 220–230 K.

polymer forms in a subsequent stage during further defrosting of the irradiated sample, the extreme character of the dependence of the polymer yield on the dose should be connected with a superposition of the two different polymerization processes. As seen from Figure 1, cyanogen bromide polymerizes in two significantly different temperature regions, which may be caused by different types of initiating centres.

The fact that the calorimetric measurements are performed for the sample preirradiated with different doses of -radiation makes it possible to obtain the dependence of the polymer yield on the dose against the measured heat release in different temperature regions (regions of the proposed phase transition and melting). The dependences obtained so far are given in Figure 2 (curves *2* and *3*). It is evident that with an increase in the preirradiation dose, the yield of the polymer forming in the low-temperature region quickly reaches its maximum value of ~1.5%, which does not change even at very high doses (Figure 2, curve *2*). The dependence of the yield of the polymer forming in the premelting and melting regions on the irradiation dose has an extreme character (Figure 2, curve *3*). It should be noted that a maximum value of the polymer yield and then a decrease are observed in the region of very high doses when the crystal matrix structure is already sufficiently disturbed. We assume that the suppression of the polymerization of cyanogen bromide in the melting region is connected with destruction of the crystal matrix during the radiation. Such radiation-induced destruction may lead to a sufficiently sharp increase in the molecular mobility in this temperature region.[13] The result of such changes may be an increased rate of termination of the polymer chains, which leads to a degradation of the chain process, hence to a decrease in the polymer yield.

Thus, the absence in the cyanogen bromide crystal of intermolecular chains with strong N···H hydrogen bonds typical of the HCN crystal causes a difference in the cryopolymerization dynamics between these two monomers. It is very probable that the low thermal stability of the polymer, as distinct from the polymer of hydrogen cyanide, is also connected with the absence of 'reinforcing' hydrogen bonds between macromolecules in the polymer of cyanogen bromide.

This work was financially supported by the Russian Foundation for Basic Research (grant no. 96-03-32271).

## References

1 P. S. Mozhaev, D. P. Kiryukhin, G. A. Kichigina and I. M. Barkalov, *Mendeleev Commun.*, 1994, 17.
2 P. S. Mozhaev, G. A. Kichigina, D. P. Kiryukhin and I. M. Barkalov, *Khim. Vys. Energ.*, 1995, **29**, 19 [*High Energy Chem.* (*Engl. Transl.*), 1995, **29**, 15].
3 P. S. Mozhaev, G. A. Kichigina, Z. G. Aliev, D. P. Kiryukhin, L. O. Atovmyan and I. M. Barkalov, *Dokl. Ross. Akad. Nauk*, 1994, **335**, 747 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 1994, **335**, 77].
4 D. P. Kiryukhin, G. A. Kichigina, P. S. Mozhaev and I. M. Barkalov, *Vysokomol. Soedin., Ser. A*, 1997, **39**, 1109 (*Polym. Sci. A*, 1997, **39**, 727).
5 D. P. Kiryukhin, G. A. Kichigina and I. M. Barkalov, *Vysokomol. Soedin., Ser. A*, 1998, in press.
6 S. I. Kuzina, D. P. Kiryukhin, A. P. Pivovarov, P. S. Mozhaev, A. I. Mikhailov and I. M. Barkalov, *Khim. Vys. Energ.*, 1998, in press.
7 S. I. Kuzina, P. S. Mozhaev, D. P. Kiryukhin, A. I. Mikhailov and I. M. Barkalov, *Mendeleev Commun.*, 1996, 34.
8 S. I. Kuzina, P. S. Mozhaev, D. P. Kiryukhin, A. I. Mikhailov and I. M. Barkalov, *Khim. Vys. Energ.*, 1996, **30**, 295 [*High Energy Chem.* (*Engl. Transl.*), 1996, **30**, 267].
9 S. I. Kuzina, P. S. Mozhaev, D. P. Kiryukhin, A. I. Mikhailov and I. M. Barkalov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 859 (*Russ. Chem. Bull.*, 1996, **45**, 814).
10 J. A. Platts and S. T. Howard, *J. Chem. Phys.*, 1996, **105**, 4468.
11 D. H. Gein, *Ber.*, 1934, **67**, 1028.
12 I. M. Barkalov and D. P. Kiryukhin, *Int. Rev. Phys. Chem.*, 1994, **13**, 337.
13 D. P. Kiryukhin, O. I. Barkalov and I. M. Barkalov, *Khim. Vys. Energ.*, 1995, **29**, 271 [*High Energy Chem.* (*Engl. Transl.*), 1995, **29**, 247].

*Received: Moscow, 20th February 1998*
*Cambridge, 1st May 1998; Com. 8/01641K*