Thermal Conductivity of Polyelectrolytes with Different Counterions

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Thermal Conductivity of Polyelectrolytes with Different Counterions

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ABSTRACT

Polyelectrolytes are important to many applications, such as electronics and batteries. In this work, we study the thermal conductivity of polyelectrolytes with different counterions using molecular dynamics (MD) simulations. Both anionic and cationic polyelectrolytes, including poly(acrylic acid) and poly(allylamine hydrogen halide), are investigated. We have simulated a total number of 17 polyelectrolytes with different counterions and we find that all of them have thermal conductivity values between 0.2 and 0.7 W/(m.K). By analyzing thermal conductivity against different counterion descriptors (atomic mass, atomic radius, van der Waals radius and ionic radius), we find a strong negative relationship between thermal conductivity and the ionic radii of counterions. We rationalize such a discovery through analyzing the heat flux at molecular level and find that thermal conductivity shows a general increasing trend with respect to the interatomic non-bonding forces and atomic velocities. We have also found a positive correlation between the MD-calculated thermal conductivity and that from the minimum thermal conductivity model, and this correlation can also be traced back to the same molecular level origin. Our study provides new insights to the heat transfer physics in polymers and may help scientists develop polyelectrolytes with desirable thermal conductivity.
1. INTRODUCTION

High thermal conductivity polymers are attractive to many applications, such as flexible electronic devices \(^1\)\(^-\)\(^3\) and Li-ion batteries. \(^4\)\(^,\)\(^5\) In polymers, along the molecular backbone direction heat transfer can be very efficient due to the strong covalent bonds, while in the inter-chain direction heat transfer is much less efficient due to the weak non-bonding interactions. \(^6\)\(^-\)\(^9\) A number of recent studies have revealed that polymer thermal conductivity is strongly related to its molecular level conformation. \(^6\)\(^,\)\(^8\)\(^,\)\(^10\)\(^-\)\(^14\) For example, stiffer molecular backbones can make the chains straighter even in the amorphous state \(^15\) and thus increase the amount of heat that can be transferred through the strong backbone. \(^12\) In polymer blends, it is reported that increasing the inter-chain interaction through engineering hydrogen bonds can stretch the polymer chains and enhance the thermal conductivity up to 1.5 W/(m.K). \(^6\)\(^,\)\(^8\)

In polyelectrolytes, the heat transfer mechanism can be more complicated, because the strong Coulombic interactions between the ionized polymer chain and the counterions can directly contribute to heat transfer or indirectly affect heat transfer by influencing the chain conformation. \(^14\)\(^,\)\(^16\)\(^,\)\(^17\) There are still debates on the roles of counterions in polyelectrolyte thermal conductivity. It is reported that ionized poly(acrylic acid) (PAA) at high pH can stretch the polymer backbone and reach a thermal conductivity of \(~\)1.2 W/(m.K). \(^14\) On the other hand, the counterion condensation theory indicates that at high ionization concentrations, the polymer chains in bulk PAA should be collapsed instead of stretched, \(^18\)\(^-\)\(^20\) which is also observed from molecular dynamics (MD) simulations. \(^16\) Through a parametric study in MD simulations, we previously found that the strong Coulombic interactions between the counterions and the ionized polyelectrolyte chain can enhance heat transfer through the Lennard-Jones (LJ) interactions. \(^16\) How this knowledge can be generalized to help design new materials and develop high thermal conductivity...
conductivity polyelectrolytes remain to be explored. In polyelectrolytes, it is reported that the counterion-counterion, counterion-polymer and polymer-polymer interactions are strongly related to the partial charge and the ionic size of the counterions, \(^{21-24}\) which makes the study of the role of different ions in polyelectrolyte thermal conductivity interesting.

In this work, we study the heat transfer mechanism of polyelectrolytes with different counterions using MD simulations. We have investigated 17 different polyelectrolytes in total, which includes PAA, 3 anionic and 13 cationic polyelectrolytes. We find that all of the polyelectrolytes have thermal conductivity values between 0.2 and 0.7 W/(m.K). The relationship between thermal conductivity and different counterion descriptors (atomic mass, atomic radius, van der Waals (vdW) radius, and ionic radius) are analyzed using a machine learning algorithm. The MD-calculated thermal conductivity is interpolated at molecular level through the interatomic non-bonding forces and the atomic velocities. We also compare with the minimum thermal conductivity model, using the number density and speed of sound.

2. METHODS

In this study, we have simulated cationic PAX and anionic PAHY (Fig. 1a), where X represent Li\(^+\), Na\(^+\), Mg\(^{2+}\), Al\(^{3+}\), K\(^+\), Ca\(^{2+}\), Cr\(^{3+}\), Fe\(^{2+}\), Fe\(^{3+}\), Ni\(^{2+}\), Cu\(^{2+}\), Sn\(^{2+}\), Pb\(^{2+}\), and Y represent F\(^-\), Cl\(^-\), Br\(^-\). The neural PAA is also studied as a reference. To prepare the simulation domain, single chains of PAA, PAX or PAHY with lengths of 50 monomers (Fig. 1a) are built using BIOVIA Materials Studio.\(^25\) All polyelectrolytes are fully ionized. For each polyelectrolyte, a single polymer chain is first relaxed under the NPT ensemble (600 K, 1 atm) until its volume converges. The single chain is then replicated 100 times to construct simulation domain of \(80 \times 80 \times 80 \text{ Å}^3\), which contains 100 chains and about 45,000 atoms in total. The
The thermal conductivity is calculated by the non-equilibrium MD simulation (NEMD) method at 300 K and 1 atm. Figure 1b shows the schematic of the NEMD setup. Using Langevin thermostats, a heat source of 10 Å is applied at the center of the simulation cell, and two heat sinks of 5 Å each are applied at either edge of the cell. Periodic boundary conditions (PBC) are applied in all three directions. At steady state, the thermal conductivity \( (k) \) is calculated by Fourier’s law \( (k = -J/\nabla T) \), where heat flux \( (J) \) is determined from the energy
added or subtracted by the two thermostats (Fig. S1a, supporting information (SI)) and temperature gradient ($\nabla T$) is determine from the linear fit of the temperature profile (Fig. S1b in SI). All the MD simulations are carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The interactions are described by the consistent-valence force field (CVFF), and the CVFF parameters are directly adopted from BIOVIA Materials Studio. Table S1 and Scheme S1 in the SI list the partial charges and Lennard-Jones (12-6) potential parameters of all atom types. The long-range Coulombic force is calculated by the Ewald summation method based on the particle-particle particle-mesh algorithm.

The partial charge assigned to each atom is important to the Coulombic interaction and thus can potentially impact thermal conductivity prediction for polyelectrolytes. We use the Electro-Static Potential (ESP) fitting method in Gaussian 09 to calculate the partial charges from the first-principles density functional theory for two representative cases, including PAA and PANa. After all charges are calculated, the average value over all atoms in the same type is used for that type of atom. Tables S2 and S3 in the SI list the comparison of the ESP and CVFF partial charges. However, our results (Fig. S4 in SI) show that such adjusted partial charges do not alter the predicted thermal conductivity beyond the error bars in comparison to the CVFF charges, which were empirically assigned. We thus use the CVFF charges for all the rest simulations.

3. RESULTS AND DISCUSSIONS

Figure 2 shows the thermal conductivity values of all polyelectrolytes with different counterions simulated in this study, and the x-axis represents the atomic number of the counterions. It is shown that all the polyelectrolytes have thermal conductivity values between
0.2 - 0.7 W/(mK), which fall in the same range as experimentally measured data.\textsuperscript{33,34} At the molecular level, thermal transport is due to atoms transferring energy from one to another via interatomic forces. The heat flux along the x-axis can be written as:

\[
J_x = \frac{1}{V} \left\{ \sum_i v_{x,i} * e_i + \frac{1}{2} \sum_i \sum_{<j} f_{ij} * \left( \vec{v}_i + \vec{v}_j \right) * \vec{r}_{x,ij} \right\}
\]  

(1)

where \( V \) is the volume of the simulation domain, \( v_{x,i} \) is the velocity of atom \( i \) along the x-axis, \( e_i \) is the kinetic energy of atom \( i \), \( f_{ij} \) is the pairwise interaction force between atoms \( i \) and \( j \), \( \vec{v}_i \) and \( \vec{v}_j \) are the velocity vectors of atoms \( i \) and \( j \), and \( \vec{r}_{x,ij} \) is the interatomic distance along the x-axis. Only the two-body forces are included in Eq. (1), since interactions involving counterions, including LJ and Coulombic forces, are both two-body interactions. It is also noted that the first term in Eq. (1), which corresponds to energy convection and it, is usually very small for solid polymers as atoms do not drift significantly at solid state. Equation (1) tells us that larger interatomic forces or higher atomic velocities will lead to an increase in heat transfer. In generally, we see that counterions with larger charges tend to enable higher thermal conductivity. For example, polyelectrolytes with +3 charge counterions (\textit{i.e.}, \( Al^{3+}, Cr^{3+}, Fe^{3+} \)) are on the top of Fig. 2 (green triangles) and thermal conductivity of \( Fe^{3+} \) polyelectrolyte is \(~0.1\) W/(mK) higher than that of \( Fe^{2+} \) polyelectrolyte. It can be explained as that larger charges can lead to stronger Coulombic interactions and thus increase thermal conductivity. However, there are exceptions, for example \( Ca^{2+} \) shows lower thermal conductivity than \( K^+ \). From Eq. (1), we would also expect thermal conductivity to decrease when atoms become heavier (\textit{i.e.}, larger atomic number), since they will lead to slower atomic velocity at the same temperature. In general, we do see such trends for negative ions (\textit{i.e.}, \( F^-, Cl^- \) and \( Br^- \)) and some positive ions, but there are also exceptions (\textit{e.g.}, +3 charged ions). While some weak trends are observed, it is apparent that these influencing factors are convoluted.
Figure 2. Thermal conductivity of polyelectrolytes with different counterions. The x-axis is the atomic number of the corresponding counterions. Ions with different charges are labeled as different symbols. PAA thermal conductivity is also plotted as a reference. Since PAA does not have a counterion, hydrogen atom is regarded as its counterion.

We then further explore the relationships between thermal conductivity and important features of the counterions, including atomic mass, atomic radius, vdW radius, and ionic radius. To do this, we first use Random Forest, a machine learning technique, to quantify the feature importance of these ionic descriptors (see Section 3 in the SI for details). From this analysis, we find that ionic radius has a much higher feature importance coefficient of 0.218 than the other three features (atomic mass: 0.137; atomic radius: 0.081; vdW radius: 0.067). We then separately plot the thermal conductivity against these 4 features. Figure 3a shows thermal conductivity as a function of the counterion atomic mass. Since the atomic mass is proportional to the atomic number, the trend here is the same as that in Fig. 2, thermal conductivity generally decreases as the atomic mass increases. However, there is a cluster of data points around atomic mass below 75 amu that do not necessarily follow this general trend (e.g., ions with +3 charge).
Figure 3b shows the relationship between thermal conductivity and atomic radii of counterions, and it does not show any obvious trend. Similarly, the vdW radius does not have an obvious impact on thermal conductivity either (Fig. 3c). However, we find that thermal conductivity is strongly correlated to ionic radii of the counterions as shown in Fig. 3d, and it is generally true that counterions with larger ionic radii lead to lower thermal conductivity values. These observations agree well with the feature importance ranking from the Random Forest analysis.

**Figure 3.** Relationships between polyelectrolytes thermal conductivity and counterion (a) atomic mass, (b) atomic radius, (c) vdW radius, and (d) ionic radius. PAA is plotted as a reference. For different counterions, the atomic radii, vdW radii and ionic radii data are adopted from references [35-37] and parameters are listed in Table S4 (SI).
The ionic radius describes the effective size of the counterion due to interatomic interactions with other atoms, which includes vdW and Coulombic forces. It is natural to believe that smaller ionic radii would result in shorter interaction distances between the counterion and the ionized groups on polymer, as a result these distances should also show similar correlation with thermal conductivity as the ionic radii. We then calculate the radial distribution function (RDF) of the ionized oxygen atoms of the polymer around the cations and the ionized nitrogen atoms around the anions (see section 4 in SI). The position of the first peak in such RDF profiles (listed in Table S5 in SI) should be correlated to the ionic radii,\textsuperscript{16,39,40} and thus we use the first peak position as another feature. From the same Random Forest feature importance evaluation, the first RDF peak has an importance coefficient of 0.227, which similar to that of the ionic radius and much higher than those of other features. As shown in Fig. 4a, the thermal conductivity generally decreases with the increasing the first peak location of RDF.

**Figure 4.** Relationships between polyelectrolytes thermal conductivity and (a) the first RDF peak positions of the cation-oxygen (or anion-nitrogen) atoms, (b) the counterion atomistic heat flux from the LJ interactions. PAA is plotted as a reference only. The RDF peak position values are also listed in Table S5 (SI).
Furthermore, according to our previous study, the fundamental mechanism of thermal conductivity enhancement in polyelectrolytes is related to the Coulombic interaction attracting the atoms closer between counterions and the ionized polymer groups, which enlarges LJ forces the atoms experience around their equilibrium distances. According to Eq. (1), this larger LJ forces, when acting on lighter atoms with higher velocities, should result in higher heat flux and thus improve thermal conductivity. We have extracted the LJ portion of the interatomic forces at the equilibrium distances of different cations interacting with the oxygen atoms in the polymer molecule, and the same LJ forces are calculated between anions and the nitrogen atoms (see Fig. S6 in SI). We note that all the LJ forces are in the strong repulsive region, which is constant with our previous parametric study. In the repulsive region, the LJ potential curves have much larger slopes, which correspond to the amplitude the forces, than that in the attractive region. When the Coulombic interactions between oppositely charged atoms are stronger, they can attract atoms closer together, the LJ force tends to be deeper in the repulsive region and thus induce larger LJ forces. The other factor, atomic velocity ($v$), is inversely related to the atomic mass ($m$) considering the relation between temperature ($T$) and kinetic energy ($\frac{1}{2}mv^2 \propto T = constnat$ and thus $v \propto 1/\sqrt{m}$), according to the kinetic theory. In addition, Eq. (1) also involves a double summation over all interacting pairs, which should scale with $n^2$ ($n$ is the number density explicit hydrogen atoms), and the interatomic distance ($r_{ij}$), which should scale with the RDF peak location ($d_{RDF}$). Following the above argument, we evaluate the feature importance of the combined parameter ($n^2F_{LJ}d_{RDF}/\sqrt{m}$ is the atomistic heat flux), involving the equilibrium LJ force ($F_{LJ}$), atomic mass ($m$), number density ($n$) and RDF peak location ($d_{RDF}$). The feature importance of this new parameter has a relatively high coefficient of 0.207 (Table S4 in SI).
Figure 4b shows the plot of thermal conductivity against this new parameter and it shows a generally increasing trend.

The above analysis is based on physical reasoning at the molecular level. In literature, Xie et al. have used the minimum thermal conductivity model, Eq. (2), \(^{33,34}\) to analyze the polyelectrolyte thermal conductivity in their experiments,

\[
k_{min} = \left(\frac{\pi}{4B} \right)^{1/3} k_B \left(\frac{2}{3} n\right)^{2/3} (V_l + 2V_t)
\]

where \(k_B\) is the Boltzmann constant, \(n\) is the atomic number density explicit hydrogen atoms, and \(V_l\) and \(V_t\) are respectively the longitudinal and transverse speeds of sound. In our study, \(V_l\) and \(V_t\) are calculated from the bulk modulus and shear modulus using MD simulations (Table S6 in SI). Table 1 lists the \(n\), \(V_l\), \(V_t\) and thermal conductivity (\(k_{min}\) and \(k_{MD}\)) values for comparison. We plot our MD-calculated thermal conductivity values against \(n^{2/3}\) and \(V = \frac{1}{3} (V_l + 2V_t)\), in Figs. 5a and 5b respectively. It shows that general increasing trends can be obvious in both relations. The number density is proportional to the number of vibrational modes in a unit volume and thus it is related to the volumetric heat capacity. When heat capacity is larger, thermal conductivity tends to be larger. Meanwhile, when the heat carriers have higher propagation speeds, thermal conductivity should also increase.
**Figure 5.** MD-calculated thermal conductivity as a function of (a) atom number density, (b) average speed of sound. (c) Thermal conductivity values calculated from MD simulations compared with that from the minimum thermal conductivity model.

**Table 1.** The number density \( n \) (explicit hydrogen atoms), speed of sound (longitude \( V_{l} \) and transverse \( V_{t} \)), thermal conductivity values from the minimum thermal conductivity model \( k_{min} \) and from this MD simulation study \( k_{MD} \).

| Polyelectrolytes | \( n \) (number/Å\(^3\)) | \( V_{l} \) (m/s) | \( V_{t} \) (m/s) | \( k_{min} \) (W/(m.K)) | \( k_{MD} \) (W/(m.K)) |
|------------------|--------------------------|-----------------|----------------|-----------------------|-----------------------|
| PAA              | 0.057                    | 4616            | 2258           | 0.574                 | 0.307                 |
| PALi             | 0.059                    | 7456            | 3815           | 0.968                 | 0.613                 |
| PANa             | 0.062                    | 6395            | 3440           | 0.844                 | 0.667                 |
| PAMg             | 0.059                    | 6577            | 3225           | 0.834                 | 0.544                 |
| PAAI             | 0.061                    | 6833            | 3610           | 0.921                 | 0.609                 |
| PAK              | 0.054                    | 6624            | 3562           | 0.833                 | 0.510                 |
| PACa             | 0.068                    | 6311            | 2936           | 0.858                 | 0.429                 |
| PACr             | 0.065                    | 6856            | 3515           | 0.958                 | 0.690                 |
| PAFep{superscript:2+} | 0.066                | 6818            | 3567           | 0.968                 | 0.609                 |
| PAFe{superscript:3+} | 0.067                | 6960            | 3544           | 0.983                 | 0.696                 |
| PANi             | 0.067                    | 6540            | 3028           | 0.879                 | 0.644                 |
| PACu             | 0.067                    | 6407            | 3019           | 0.867                 | 0.596                 |
| PASn             | 0.062                    | 5044            | 2525           | 0.668                 | 0.401                 |
| PAPb             | 0.061                    | 5013            | 2470           | 0.651                 | 0.334                 |
| PAHF             | 0.050                    | 6772            | 3512           | 0.790                 | 0.610                 |
| PAHCl            | 0.031                    | 6678            | 4167           | 0.635                 | 0.316                 |
| PAHBr            | 0.030                    | 5455            | 3452           | 0.507                 | 0.229                 |
Figure 5c further shows the MD-calculated thermal conductivity \( (k_{MD}) \) against the minimum thermal conductivity \( (k_{min}) \). It is found that \( k_{MD} \) are uniformly lower than \( k_{min} \). This over estimation of the minimum thermal conductivity model was also observed when compared to experimental data of polyelectrolytes, which was explained by the over estimation of thermally excited vibrational modes at 300 K in the minimum thermal conductivity model.\(^{33}\) We also note that our MD-calculated thermal conductivity is not necessarily comparable to the experimental data,\(^{14,33,34}\) since the polyelectrolytes materials in experiments have unknown degrees of ionization, which was shown to impact thermal conductivity.\(^{16}\) However, there is a very strong positive correlation between \( k_{MD} \) and \( k_{min} \) as shown in Fig. 5c, meaning that the minimum thermal conductivity model, Eq. (2), should also be able to be interpreted from the molecular features as for the MD-calculated thermal conductivity. A higher atomic number density implies that there are more pairs of interatomic interactions in a unit volume, which can result in a larger heat flux according to Eq. (1). A higher speed of sound suggests either smaller atomic masses or stronger interatomic forces, or both. According to our previous discussion, smaller atomic masses can lead to higher atomic velocities, which can in turn increase thermal conductivity according to Eq. (1). Similarly, stronger interatomic forces can also lead to more efficient thermal transport according to Eq. (1). It turns out that although with distinct origins, \( k_{MD} \) and \( k_{min} \) can be unified using the same molecular level theory.

4. CONCLUSIONS

In summary, we use MD simulations to calculate the thermal conductivity of polyelectrolytes with different counterions. We find that all amorphous polyelectrolytes have a
thermal conductivity between 0.2 and 0.7 W/(m.K), and the calculated values are analyzed against descriptors of counterions (atomic mass, atomic radius, vdW radius and ionic radius). We find a strong relationship between thermal conductivity and ionic radii of counterions, and we are able to rationalize such an observation using the molecular level heat flux expression. Through physical reasoning, we find that the atomic number density, LJ force, RDF peak position and the atomic mass can form a combined factor that can reasonably explain the thermal conductivity trend of polyelectrolytes with different counterions. The MD-calculated thermal conductivity \( k_{MD} \) is also found correlate well with that predicted by the minimum thermal conductivity model \( k_{min} \), which can also be explained by the theory at molecular level. The results from this work may provide useful insight to polymer thermal transport physics and important guidance to engineering polyelectrolytes with desirable thermal conductivity.

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Notes
The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information (SI) includes the following content: detailed information about simulation models and methods and additional simulation results.

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Supporting Information for:

Thermal Conductivity of Polyelectrolytes with Different Counterions

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1. Steady state heat flux and temperature profiles

![Graphs showing energy tally and temperature profile](image)

**Figure S1.** (a) The energy tally recorded at two thermostats for calculating the heat flux. (b) The temperature profile along the heat flux direction at steady state.
Table S1. The atomic weight, partial charge, LJ-$\epsilon$ and LJ-$\sigma$ parameters of counterions in different polyelectrolytes.

| Counterion Type | Atomic weight | Partial charge | LJ-$\epsilon$ (kcal/mol) | LJ-$\sigma$ (Å) |
|-----------------|---------------|----------------|--------------------------|----------------|
| PAA H           | 1             | 0.35           | 0                        | 0              |
| PALi Li         | 6.94          | 1              | 4.735                    | 2.839          |
| PANa Na         | 22.99         | 1              | 1.60714                  | 1.89744        |
| PAMg Mg         | 24.305        | 2              | 0.0400184                | 4.05343        |
| PAAI Al         | 26.982        | 3              | 0.114068                 | 4.13567        |
| PAK K           | 39.102        | 1              | 5.451                    | 3.197          |
| PACa Ca         | 40.0798       | 2              | 0.121235                 | 2.81295        |
| PACr Cr         | 51.996        | 3              | 11.575                   | 2.336          |
| PAFe2+ Fe       | 55.847        | 2              | 12.138                   | 2.321          |
| PAFe3+ Fe       | 55.847        | 3              | 12.138                   | 2.321          |
| PANi Ni         | 58.71         | 2              | 11.983                   | 2.282          |
| PACu Cu         | 63.546        | 2              | 9.439                    | 2.338          |
| PASn Sn         | 118.69        | 2              | 1.60714                  | 1.89744        |
| PAPb Pb         | 207.2         | 2              | 5.451                    | 3.197          |
| PAHF F          | 18.9984       | -1             | 0.0687685                | 3.08081        |
| PAHCl Cl        | 35.453        | -1             | 0.107                    | 4.4463         |
| PAHBr Br        | 79.904        | -1             | 0.09                     | 4.62376        |
Scheme S1. The symbols of all types of atoms are marked for PAA, PANa and PAHCl. The partial charge, LJ-ε and LJ-σ parameters are listed for different atom types in polyelectrolytes.
2. Electro-Static Potential (ESP) fitting for partial charge and its impact on thermal conductivity

The ESP fitting method in Gaussian 09 \(^1\) is used for the partial charge redistribution calculation in PAA and PANa. A single polyelectrolyte molecule is first built in GaussView. Then, we optimize the initial molecular geometry by Gaussian 09. After optimization, the ESP charge for every atom on the molecule is calculated by Gaussian 09 with code \#B3LYP/6-31g* pop=mk iop(6/50=1). Since we are not able to calculate the whole polymer chain with 50 monomers, we calculate the ESP charges for PAA and PANa chains from 1 monomer to 7 monomers. Each atom has a different ESP charge in our calculation, and it is important that we follow the CVFF model and classify all the atoms into 7-8 types (Scheme S1). An average partial charge value is calculated for each atom type. Figure S2 shows that when the number of monomers is more than 5, the ESP charges converge for both PAA and PANa. Figure S3 shows the calculated ESP charges for each atoms on PAA and PANa for the 5 monomers. Tables S2 and S3 list the comparison of ESP-PAA and CVFF-PAA, ESP-PANa and CVFF-PANa partial charges.

![Figure S2](image)

**Figure S2.** The ESP partial charge of all types of atoms converges when the number of monomers increases from 1 to 7 in (a) PAA and (b) PANa. The atom symbols are consistent with Scheme S1.
Figure S3. The ESP partial charges for each atom are marked on the schemes at a chain length of 5 monomers in (a) PAA and (b) PANa.

Table S2. The partial charges in PAA from ESP calculation and CVFF are listed. The atom symbols are consistent with Scheme S1.

| Atom type | Symbol | CVFF-PAA Charge (e) | ESP-PAA Charge (e) |
|-----------|--------|---------------------|--------------------|
| 1         | c3     | -0.3                | -0.2064            |
| 2         | h      | 0.1                 | 0.0688             |
| 3         | c1     | -0.1                | -0.0688            |
| 4         | c'     | 0.41                | 0.4575             |
| 5         | o'     | -0.38               | -0.44245           |
| 6         | oh     | -0.38               | -0.44245           |
| 7         | ho     | 0.35                | 0.4274             |
| 8         | c2     | -0.2                | -0.1376            |
Table S3. The partial charges in PANa from ESP calculation and CVFF are listed. The atom symbols are consistent with Scheme S1.

| Atom type | Symbol | CVFF-PANa Charge (e) | ESP-PANa Charge (e) |
|-----------|--------|----------------------|---------------------|
| 1         | c3     | -0.3                 | -0.2261             |
| 2         | h      | 0.1                  | 0.0057              |
| 3         | c1     | -0.1                 | 0.102               |
| 4         | c-     | 0.14                 | 0.6627              |
| 5         | o-     | -0.57                | -0.7807             |
| 6         | c2     | -0.2                 | -0.2204             |
| 7         | Na     | 1                    | 1                   |

Figure S4 shows the thermal conductivity for polyelectrolytes with both CVFF and ESP partial charges. Figure S4a shows that the thermal conductivity of ESP-PAA is slightly higher than that of CVFF-PAA, while the thermal conductivity of CVFF-PANa is slightly higher than that of ESP-PANa, but the values are within the error bars of each other. We thus choose to use CVFF charges for the rest of the study.

Figure S4. Thermal conductivity comparisons between polyelectrolytes with CVFF and ESP partial charges redistributions for PAA and PANa.
3. Random Forest for feature importance quantification

We use random forest to quantify the relationship between descriptors and thermal conductivity, and then calculate the feature importance score based on the fitted model. The random forest consists of different number of trees, which split dataset into branches using provided features until each leaf node of the tree contains highly homogeneous entries. The number of tree nodes that use certain feature to reduce the impurity is used to define the feature importance measurement, which is then weighted by the associated number of training samples in each node. The hyper-parameters are optimized before all feature importance calculations. The package Scikit-learn \(^2\) is used for random forest implementation and feature importance calculation. Table S4 lists the feature importance of each descriptor.

**Table S4.** The feature importance of each descriptor.

| Descriptor                                      | Feature importance |
|------------------------------------------------|--------------------|
| Atomic mass \((m)\)                            | 0.13736613         |
| Atomic radius                                  | 0.08071151         |
| vDW radius                                     | 0.0665994          |
| Ionic radius                                    | 0.21804478         |
| LJ force at equilibrium position \((F_{LJ})\)  | 0.04299934         |
| The 1st RDF peak position \((d_{RDF})\)        | 0.22656575         |
| Number density \((n)\)                         | 0.02072037         |
| \(n^2F_{LJ}d_{RDF}/\sqrt{m}\)                 | 0.20699272         |
4. Radial distribution function with respect to counterions

The first peak of the radial distribution function (RDF) is related to the interaction distance from the polymer chain to the counterions. Figure S5 shows the RDF plots of cation-oxygen or anion-nitrogen atoms for different polyelectrolytes and the first cation-oxygen or anion-nitrogen RDF peak positions are listed in Table S4. Table S4 also lists the atomic number, atomic radius, vDW radius and ionic radius of each counterion.

**Figure S5.** The RDF plots for cation-oxygen (or anion-nitrogen) atoms in polyelectrolytes with (a) positive charged monovalent counterions, (b) positive charged divalent counterions, (c) positive charged trivalent counterions, and (d) negative charged monovalent counterions. The PAA hydrogen on COOH-oxygen RDF is plotted as a reference.
Table S5. The counterions atomic numbers, atomic radii, ionic radii, vdW radii and (cation-oxygen or anion-nitrogen) RDF first peak positions for different polyelectrolytes.

| Polymer | Atomic numbers | Atomic radii (Å) | Ionic radii (Å) | vdW radii (Å) | RDF peaks (Å) |
|---------|----------------|------------------|-----------------|---------------|---------------|
| PAA     | 1              | 0.25             | 1               | 1.1           | 1.775         |
| PALi    | 3              | 1.45             | 0.76            | 1.82          | 2.825         |
| PANa    | 11             | 1.8              | 1.02            | 2.27          | 2.375         |
| PAMg    | 12             | 1.45             | 0.72            | 1.73          | 2.825         |
| PAAI    | 13             | 1.18             | 0.535           | 1.84          | 2.875         |
| PAK     | 19             | 2.2              | 1.38            | 2.75          | 3.025         |
| PACa    | 20             | 1.94             | 1.0             | 2.31          | 2.325         |
| PACr    | 24             | 1.66             | 0.615           | 2.0           | 2.425         |
| PAFe2+  | 26             | 1.56             | 0.78            | 2.1           | 2.575         |
| PAFe3+  | 26             | 1.56             | 0.645           | 2.1           | 2.425         |
| PANi    | 28             | 1.49             | 0.7             | 1.63          | 2.575         |
| PACu    | 29             | 1.45             | 0.73            | 1.4           | 2.575         |
| PASn    | 50             | 1.45             | 1.18            | 2.17          | 2.175         |
| PAPb    | 82             | 1.54             | 1.19            | 2.02          | 2.925         |
| PAHF    | 9              | 0.42             | 1.33            | 1.47          | 2.575         |
| PAHCl   | 17             | 0.79             | 1.81            | 1.75          | 3.375         |
| PAHBr   | 35             | 0.94             | 1.96            | 1.85          | 3.425         |
5. Lennard-Jones force at equilibrium interatomic distances

As the dominant interaction is between the counterions and oxygen or NH$_3$ group, Fig. S6 shows the potential energy, total force and LJ force between counterions and the oxygen or NH$_3$ group. At the energy minimum positions, i.e., equilibrium positions (Fig. S6a), the total force equals zero (Fig. S6b). Using the equilibrium positions, we find the LJ interaction forces (Fig. S6c), which are in the strong repulsive region.

**Figure S6.** (a) The potential energy and (b) the force of the non-bonding interactions between counterions and ionized groups in polymer; and (c) the LJ force at equilibrium distances.
6. Calculated polyelectrolyte density, chain conformation and moduli

Table S6. The density, chain $R_g$, bulk modulus and shear modulus of all the polyelectrolytes.

| Polyelectrolytes | Density (g/cm$^3$) | $R_g$ (Å) | Bulk modulus (GPa) | Shear modulus (GPa) |
|------------------|--------------------|----------|-------------------|---------------------|
| PAA              | 1.34               | 12.0     | 19.47             | 6.84                |
| PALi             | 1.27               | 14.2     | 45.94             | 18.47               |
| PANa             | 1.76               | 12.5     | 44.28             | 20.86               |
| PAMg             | 1.47               | 12.4     | 43.27             | 15.31               |
| PAAI             | 1.51               | 15.5     | 44.30             | 19.69               |
| PAK              | 1.64               | 14.3     | 44.31             | 20.85               |
| PACa             | 1.86               | 12.6     | 52.68             | 16.02               |
| PACr             | 1.80               | 10.0     | 54.99             | 22.27               |
| PAFe2+           | 1.97               | 11.9     | 58.27             | 25.13               |
| PAFe3+           | 1.87               | 9.4      | 59.21             | 23.46               |
| PANi             | 2.02               | 13.4     | 61.73             | 18.53               |
| PACu             | 2.07               | 12.0     | 59.69             | 18.83               |
| PAsn             | 2.42               | 12.3     | 41.05             | 15.45               |
| PAPb             | 3.19               | 13.4     | 54.24             | 19.47               |
| PAHF             | 1.19               | 9.8      | 35.08             | 14.70               |
| PAHCl            | 0.99               | 11.7     | 21.21             | 17.18               |
| PAHBr            | 1.39               | 12.8     | 19.33             | 16.61               |

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