

# A semi-quantitative tribo-electric series for polymeric materials: the influence of chemical structure and properties

A.F. Diaz<sup>a,\*</sup>, R.M. Felix-Navarro<sup>b</sup>

<sup>a</sup> *Department of Chemical and Materials Engineering, San Jose State University, One Washington Square, San José, CA 95192, USA*

<sup>b</sup> *Instituto Tecnológico de Tijuana, Centro de Graduados e Investigación, A. P. 1166, 22000 Tijuana, Baja California, Mexico*

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## Abstract

A semi-quantitative tribo-charging series that includes a wide range of synthetic and natural polymers was constructed by combining four qualitative triboelectric series from literature reports plus quantitative charging results with metal contacts. This not only connects the results from different laboratories but it also provides a series with a wide variety of polymeric materials which can be used to estimate their relative charging capacity. The ordering of the polymers in the series suggests that the charging develops from the transfer of protons between the contacting surfaces.

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## 1. Introduction

Contact electrification, also known as static electricity or contact charging, is the process that produces surface charges on dissimilar materials when they are contacted and separated. During this contact, each material develops a charge of opposite polarity. Contact electrification is a complicated process where both the

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\*Corresponding author. Tel.: +1-408-9243944; fax: +1-408-9244057.

E-mail address: [adiaz@email.sjsu.edu](mailto:adiaz@email.sjsu.edu) (A.F. Diaz).

magnitude and polarity of the developed charge is sensitive to the material composition, the contact process and the environmental conditions. It is important to understand the charging behavior because charging is a common occurrence in many manufacturing environments. In some circumstances, it is a key performance factor, while in others, it is an undesirable problem where the build up of static electricity can result in product failure or a serious safety hazard.

Contact electrification is known to be a highly irreproducible phenomenon [1]. This arises in part because many factors influence the contact charge that develops on a polymer, such as, the surface characteristics, the experimental conditions and nature of contact. Since the charge transfer is an interfacial phenomenon, the chemical composition and surface roughness affect the charge. Pre-treatments, contaminant level and the general history of the material are all important considerations. Ambient conditions also affect the charge, where a higher charge is often attained in vacuum than in the atmosphere and the charge is significantly reduced when the humidity is high.

Besides the obvious effects of the contact pressure, the nature of the contact also influences the magnitude of the charge. The contact can be a single (or multiple) contacts at a designated site on the surface of the material with no translational motion along the surface, or there can be translational motion, such as, rubbing or sliding. In the latter case, contact area is greater and other complications such as friction and physical or chemical damage may accompany the charge transfer.

## 2. *Triboelectric series*

The charging process is well understood for metals and is attributed to the transfer of electrons from the metal to the accompanying material. Charging that occurs with polymers is not as easily explained and this is unfortunate because the charging behavior must be understood to properly control the charge that may develop on these materials. On the other hand, there are several consistent charging patterns observed with these materials. In particular, insulators [2] and organic polymers [3–6] can be arranged in a “triboelectric series” which lists the materials in the order of the relative polarity of the contact charge acquired, from those that charge most positive, like nylon, to those that charge most negative, like the halogenated polymers. In the triboelectric series the higher positioned materials will acquire a positive charge when contacted with a material at a lower position along the series. Thus, the triboelectric series can be used to estimate the relative charge polarity of the materials.

A search of the literature identified four triboelectric series which were published by different laboratories during a time span of 90 years, 1898–1987. Tribo-series were published by Coehn [3] in 1898, by Hersh and Montgomery [4] in 1955, by Henniker [5] in 1962 and by Adams [6] in 1987. These are listed in Table 1, and the polymeric materials that are common to each series are lined up horizontally to provide cross comparisons. As can be seen, there is a wide variety of synthetic and natural polymers, and the ordering of the polymers is remarkably similar in every series.

Table 1  
Comparison of four published triboelectric series

Ref. [3]	Ref. [4]	Ref. [5]	Ref. [6]
<b>Positive charge</b>			
		Silicone elastomer with silica filler	Air
		Borosilicate glass, fire polished	Human hands
	Wool	Window glass	Asbestos
		Aniline-formol resin	Rabbit fur
		Polyformaldehyde	Glass
		<i>Polymethyl methacrylate</i>	Mica
		Etylcellulose	Human hair
		Polyamide 11	
Nylon 6,6	Nylon	Polyamide 6-6	Nylon
		Rock salt (NaCl)	Wool
		Melanime formol	Fur
		Wool, knitted	Lead
		Silica, fire polished	Silk
Cellulose	Viscose	Silk, woven	Aluminum
Cellulose acetate		Polyethylene glycol succinate	Paper
		Cellulose acetate	
		Polyethylene glycol adipate	
		Polydiallyl phthalate	
		Cellulose (regenerated) sponge	
	Cotton	Cotton, woven	Cotton
		Polyurethane elastomer	Steel
	Silk	Styrene-acrylonitrile copolymer	Wood
		Styrene-butadiene copolymer	Amber
	Acetate	Polystyrene	Sealing wax
Polymethyl methacrylate	Lucite	Polyisobutylene	Hard rubber
Polyacetate	Polyvinyl alcohol	Polyuretane flexible sponge	Nickel, Copper
	Dacron	Borosilicate glass, ground state	Brass, Silver
Polyethylene terephthalate		Polyethylene glycol terephthalate	Gold, Platinum
		Polyvinyl butyral	Sulfur
		Formo-phenolique, hardened	Acetate, Rayon
		Epoxide resin	Polyester
		Polychlorobutadiene	Styrene (Styrofoam)
	Orlon	Butadiene-acrylonitrile copolymer	Orlon
		Natural rubber	Saran
Polyacrylonitrile		Polyacrilonitrile	
<i>Polyvinyl chloride</i>	<i>Polyvinyl chloride</i>	Sulfur	

Table 1 (continued)

Ref. [3]	Ref. [4]	Ref. [5]	Ref. [6]
Polybisphenol carbonate	Dynel		
Polychloroether	Velon		Polyurethane
Polyvinylidene chloride			
Poly(2,6-dimethyl polyphenylene oxide)			
<i>Polystyrene</i>			
<i>Polyethylene</i>	<i>Polyethylene</i>	Polyethylene	Polyethylene
<i>Polypropylene</i>		Polydiphenylol propane carbonate	Polypropylene
		Chlorinated polyether	
		Polyvinyl chloride with 25% DOP	Vinyl (PVC)
		Polyvinyl chloride without plasticizer	Silicon
		Polytrifluorochloroethylene	
		Polytetrafluoroethylene	Teflon
		Polytetrafluoroethylene	Teflon
Negative charge			

These triboelectric series are again listed in Table 2, however, only the organic polymers are included, while the inorganic materials and metals were removed. The similarity in the ordering is now more obvious. Nylon falls at the positive end of each series and polytetrafluoroethylene at the negative end. There are surprisingly few inconsistencies in the ordering of the polymers between the different series. In fact, only 3 out of the 52 polymers listed have inconsistent positions. These are the position of polyvinyl chloride in columns 1 and 2 versus column 3, the position of wool and silk in column 2 versus column 3 and 4, and the position of polymethyl methacrylate in column 1 versus column 3. These polymers are printed in italic type, both in Tables 1 and 2. The correspondence in the order of the polymers published by the different laboratories is remarkable considering that the reports appeared during a time span of 90 years, plus the fact that details provided about the experimental materials, procedures and conditions are minimal. In fact, in some cases no details are reported. Finally, these reports provide little or no explanation regarding the relationship between the positions and the chemical structure of the polymers. Nevertheless, it is clear that one series can be considered which accommodates the trends from the different laboratories.

Unfortunately, the triboelectric series are not quantitative and this limits their utility. A semi-quantitative series would certainly provide a better indication of the

Table 2

Reduction of four published triboelectric series for organic polymer

Ref. [3]	Ref. [4]	Ref. [5]	Ref. [6]
<b>Positive charge</b>			
	<i>Wool</i>	Aniline-formol resin Polyformaldehyde <i>Polymethyl methacrylate</i> Ethyl cellulose Polyamide 11	
Nylon 6,6	Nylon	Polyamide 6-6 Melanime formol Wool, knitted Silk, woven	Nylon Wool Silk
Cellulose	Viscose	Polyethylene glycol succinate	
Cellulose acetate		Cellulose acetate Polyethylene glycol adipate Polydiallyl phthalate Cellulose (regenerated) sponge	Paper
	Cotton	Cotton, woven Polyurethane elastomer	Cotton
	<i>Silk</i>	Styrene-acrylonitrile copolymer Styrene-butadiene copolymer	
			Wood Hard rubber Acetate, rayon
Polymethyl methacrylate	Acetate Lucite		
	Polyvinyl alcohol Dacron		Polyester Styrene (Styrofoam)
		Polystyrene Polyisobutylene Polyurethane flexible sponge	
Polyacetate Polyethylene terephthalate		Polyethylene glycol terephthalate Polyvinyl butyral Formo-phenolique, hardened Epoxide resin Polychlorobutadiene Butadiene-acrylonitrile copolymer Natural rubber Polyacrilonitrile	
Polyacrylonitrile	Orlon		Orlon
<i>Polyvinyl chloride</i>	<i>Polyvinyl chloride</i>		

Table 2 (continued)

Ref. [3]	Ref. [4]	Ref. [5]	Ref. [6]
	Dynel		
	Velon		
Polybisphenol carbonate			
Polychloroether			
Polyvinylidene chloride			Saran
			Polyurethane
Poly(2,6-dimethyl polyphenylene oxide)			
Polystyrene			
Polyethylene	Polyethylene	Polyethylene	Polyethylene
Polypropylene			Polypropylene
		Polydiphenyl propane carbonate	
		Chlorinated polyether	
		Polyvinylchloride with 25% DOP	
		Polyvinylchloride no plasticizer	Vinyl (PVC)
		Polytrifluorochloroethylene	Silicon
		Polytetrafluoroethylene	Teflon
		Polytetrafluoroethylene	Teflon
Negative charge			

charging capacity of the polymers, and would be more useful for anticipating contact charges.

3. Semi-quantitative triboelectric series

To develop a quantitative component to the triboelectric series, literature reports on contact charging with polymers were reviewed, combined with the triboelectric series listed in Table 1 to construct a semi-quantitative series. For our objectives, the most informative reports were published by four laboratories between 1974 and 2001 [7–11]. The charging data selected from these reports were obtained using multiple contacts on polymer films. The contacts were made using a spherical probe, 0.2–0.6 cm diameter, made of either Au, Pt, Al or Mg and a planar polymer sample. The polymer specimens were either solvent cast or commercial materials. The thicknesses of the polymer specimens were in the range 0.02–44 mm.

With regards to the experimental conditions, the results reported by Lowell et al. [9,10], and by Akande and Adedoyin [8] were obtained using 0.2, 0.3 and 0.6 cm

diameter spheres, respectively, of either Au, Pt, Al or Mg. The measurements were carried out using approximately 1.5 N contact force [8], and were in vacuum ( $10^{-4}$ – $10^{-5}$  Torr). The charge values reported were the average of cumulative contacts made at different locations along the polymer specimen. The number of contacts used by each laboratory was different but sufficient to produce the saturation charge. The results reported by Charlson et al. [10] were obtained using an aluminum probe in a nitrogen atmosphere. The results reported by Wählin and Bäckström [11] were obtained differently. In this case, a 0.15 cm diameter sphere of either Au, Pt, Al or Mg was slid along the planar polymer at 8 mm/s and using an 0.5 N normal force. The experiments were carried out in vacuum ( $2 \times 10^{-5}$  Torr). In every case, the charge reported was the saturation charge obtained after multiple contacts. Information on the type of contact and dimensions of the probe are provided in the table.

The polymers from these reports are listed in Table 3 in descending order of the sign and magnitude of the contact charge ( $Q$ ) produced. The charges were reported in pC which does not normalize the charge for difference in the contact area as would be the case with charge density values ( $\text{pC}/\text{cm}^2$ ). To estimate this effect of the differences in the probe sizes, the charge values were converted to charge densities assuming that only 7.5% of the total area of the spherical probe was involved in the contact. This adjustment did not effect the relative order of the materials. Therefore, we feel confident that using the charge data directly without adjusting for differences in the areas has validity for our purposes. The radii of the probes are given in the table for making this adjustment as needed.

Inspection of the charge generated on the polymers reveals trends that are effectively the same with each metal. This is seen in the plot in Fig. 2 of the charge developed with multiple contacts on the various polymers. The plot does not include the data for PV2P and PTFE because the high positive and negative charge produced with all the metals affect the sizing of the graph. The values for the noble metals, Au and Pt are higher than those for Al and Mg. This difference probably reflects the presence of the oxide layer on the Al and Mg surfaces. Because there is a monotonic and parallel relationship between the various metals, it seemed appropriate to select the data with one metal to make the comparison with the qualitative trends shown in Table 2. The data with Au was used for this purpose.

The qualitative series listed in Table 2 were combined into one and it is listed in Table 4 along with the quantitative series from Table 3. As can be seen, both series have a very similar ordering of the polymers. This combination now produces a semi-quantitative triboelectric series. The quantitative aspect of this series is based on charging generated by multiple contacts with a spherical probe in ca.  $10^{-4}$  Torr. However, the ordering of the polymers is probably very forgiving to the experimental conditions since the ordering was reproduced by several laboratories and presumably under different experimental conditions.

With the quantitative component, those polymers with conflicting positions can now be properly placed and the polymers with no measured charge values can be assigned a range of expected charge values. Many polymeric materials charge similarly such that the relative order between materials closely placed in the series will depend on the history and handling of the material.

Table 3  
Charge transfer from four metals to some polymers

Polymer  (Work function/eV) <sup>a</sup>	Charge (pC)				Type of contact	Avg. of measurement	Radius of sphere (cm)	Ref.
	Au (0.029)	Pt (−0.057)	Al (−1.18)	Mg (−1.43)				
Polyvinyl-2-pyridine (PV2P)	1.5	2.1	0.4	0.9	Multiples (400)		0.20	[7]
Polyvinyl-2-pyridine (PV2P)	16.51	13.92	12.26	10.61	Single	Not reported	0.30	[8]
Polyhexamethylene adipamide (Nylon 6.6) <sup>b</sup>	1.2	0.71	0.62	−0.25	Multiples (400)	Not reported	0.20	[7]
Polyvinyl alcohol (PVOH)	0.5	0.51	0.18	0.24	Multiples (400)	Not reported	0.20	[7]
Polyvinyl alcohol (PVOH)	1.35	1.54	0.38	17.9	Multiples (20)	Not reported	0.15	[9]
Polyvinyl acetate (PVAc)	0.20	0.22	0.13	0.08	Multiples (400)	Not reported	0.20	[7]
Polymethylmethacrylate (PMMA)	0.14	0.23	0.1	0.16	Multiples (400)	Not reported	0.20	[7]
Polymethylmethacrylate (PMMA)	3.38	3.79	1.65	−0.66	Single	Not reported	0.30	[8]
Polycarbonate (PC)	0.05	0.09	−0.02	0.52	Multiples (400)	Not reported	0.20	[7]
Polystyrene (PS)	−0.0	−0.01	−0.03	−0.06	Multiples (400)	Not reported	0.20	[7]
Polypropylene (PP)				−0.0005 <sup>a</sup>	Multiples	At least 5	0.03	[10]
Polyimide (PI)				−0.011 <sup>a</sup>	Multiples	At least 5	0.03	[10]
Polyethylene terephthalate (PET)				−0.084 <sup>a</sup>	Multiples	At least 5	0.03	[10]
Polyvinyl chloride (PVC)	−1.6	−2.8	−1.2	−1.4	Multiples (400)	Not reported	0.20	[7]
Polytetrafluoroethylene (PTFE) <sup>b</sup>	−2.8	−3.2	−3.9	−4.3	Multiples (400)	Not reported	0.20	[7]
Polytetrafluoroethylene (PTFE)	−15000 <sup>a</sup>	−15000 <sup>a</sup>	−22000 <sup>a</sup>	−26000 <sup>a</sup>	Sliding	10	0.08	[11]

All experiments were carried out in vacuum.

The polymers were prepared by solution-casting except where otherwise indicated in brackets.

<sup>a</sup> Work function reported by [8].

<sup>b</sup> Commercial sheet prepared by lapping with SiC to remove a surface layer.



Table 4

Comparison between triboelectric series generated from four published triboelectric series and a triboelectric series generated from the results of three laboratories

Triboelectric series generated from four published triboelectric series		Triboelectric series generated of results of charge of different laboratories	
Positive charge		$q$ (pC) with Au	
	Poly(vinyl-2-pyridine)		1.5
Aniline-formol resin	}		1.3–1.4
Polyformaldehyde			
Etylcellulose	}		1.2
Polyamide 11			
Polyamide 6-6	}		0.6–1.1
Melanime formol			
Wool, knitted	}		0.5
Silk, woven			
Polyethylene glycol succinate	}		0.2
Cellulose			
Cellulose acetate	}		0.15–0.19
Polyethylene glycol adipate			
Polydiallyl phthalate	}		0.14
Cellulose (regenerated) sponge			
Cotton, woven	}		Ca. 0.1
Polyurethane elastomer			
Styrene-acrylonitrile copolymer	}		0.05
Styrene-butadiene copolymer			
Wood	}		Ca. 0.025
Hard rubber			
Acetate, Rayon	}		0
<i>Polymethyl methacrylate</i> (Lucite)			
Polyvinyl alcohol	}		0
Polyester (Dacron)			
Polyisobutylene	}		0
Polyurethane flexible sponge			
Polyethylene terephthalate	}		0
Polyvinyl butyral			
Formo-phenolique, hardened	}		0
Epoxide resin			
Polychlorobutadiene	}		0
Butadiene-acrylonitrile copolymer			
Natural rubber	}		0
Polyacrilonitrile			
Acrylic fiber (Orlon)	}		0
Acrylonitrile-vinyl chloride copolymer (Dynel)			
Velon	}		0
Polybisphenol carbonate			
Polychloroether	}		0
Polyvinylidene chloride (Saran)			
Poly(2,6-dimethyl polyphenylene oxide)	}		0
<i>Polystyrene</i>			

Table 4 (continued)

Triboelectric series generated from four published triboelectric series	Triboelectric series generated of results of charge of different laboratories	
Polyethylene	Polypropylene	} ~ 0 with Brass
Polypropylene		
Polydiphenyl propane carbonate		
	Polyimide	} ~ 0 with Brass
	Polyethylene terephthalate	
Chlorinated polyether		
Polyvinyl chloride (PVC)	Polyvinyl chloride	–1.6
Polytrifluorochloroethylene		
Polytetrafluoroethylene (Teflon)	Polytetrafluoroethylene	–2.8
Negative charge		

4. Relating charging to polymer structure and properties

The question in hand is how does the charging order relate to the chemical structure of the polymers. A preliminary inspection of Table 4 reveals that

- the nitrogen containing polymers, i.e. polymers with pyridine, amine and amide groups, develop the *most positive charge* (1.2–0.5 pC),
- the halogenated polymers develop the *most negative charge* (–1.6 to –2.8 pC) and
- the hydrocarbons develop *almost no charge*.

The polymers that have oxygen functional groups charge positive but lower than the polymers that have nitrogen groups. The natural polymers, such as wool and silk, charge in the range 0.6–1.1 pC. The synthetic polymers charge in the range 0.1–0.5 pC. The nature of the oxygen group, whether it is an ether, hydroxyl or carbonyl oxygen, has only a small effect on the magnitude of the charge.

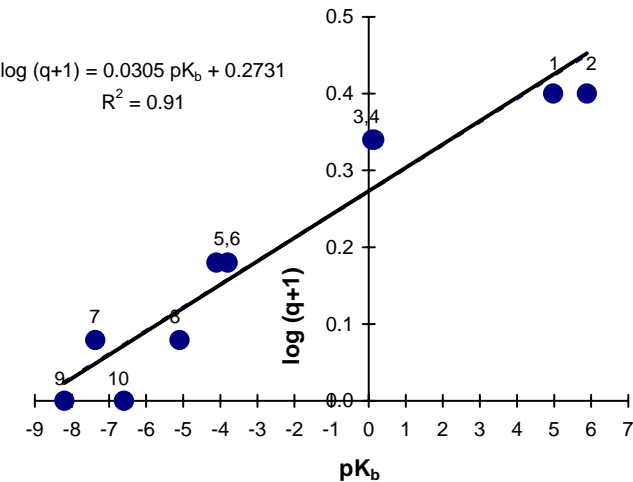
The ordering of the polymers with a low positive charge (ca. 0.1 pC) is questionable because of the inherently low magnitude of the charge plus the uncertainty in the history of the materials. The relative positions of the polymers in this group are not consistent with the expectations from the chemical structure and are not discussed further here because of the reasons given above. The chemical structures of some of the polymers in the series are shown in Table 5 along with the charge. Two reports in the literature relate the charge on polymers with the structure using derivatized polystyrenes [12]. Although the reports are qualitative, the order of the polymers resembles the order in Table 4.

Regarding the process that leads to the resulting charge, models have been proposed for an electron transfer [13–16] process where one electron is involved per event and for an ion transfer [17–19] process where a pair of electrons are involved per event. To address this issue, relationships were made with other properties of the polymers. If electron transfer is an important component of the contact charging process, some correlation between the ionization potentials and the contact charges

Table 5  
Summary of charge and chemical structure of polymers

Polymer	Chemical structure	$q/\text{Au}$ (pC)
Polyvinyl-2-pyridine (PV2P)		1.5
Polyhexamethylene adipamide (Nylon 6.6)		1.2
Polyvinyl alcohol (PVOH)		0.5
Polyvinyl acetate (PVAc)		0.2
Polymethylmethacrylate (PMMA)		0.14
Polycarbonate (PC)		0.05
Polystyrene (PS)		0.0
Polypropylene (PP)		≈0.0
Polyimide (Kapton)		≈0.0
Polyethylene terephthalate (PET)		≈0.0
Polyvinyl chloride (PVC)		-1.6
Polytetrafluoroethylene (PTFE)		-2.8

of the polymers is expected. The ionization potentials for some of these polymers are reported to be in the range  $-0.8$ – $0.4$  mJ/mol [12], and the values do not follow the trend shown in Table 4. Thus, while electron transfer has been shown to be important in metal–metal contact charging, it does not appear to be important in the charging process with organic polymers.



Compound		pK <sub>b</sub> ref. [20]	Structure of Polymer
1	2-vinyl Pyridine	4.98	
2	2-ethyl, Pyridine	5.89	
3	CH <sub>3</sub> CONH(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	0.15	
4	CH <sub>3</sub> CONHCH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	0.10	
5	Isopropanol	-4.10	
6	t-butanol	-3.80	
7	Ethyl benzoate	-7.37	
8	Ethyl acetate	-5.10	
9	Pyrene	-8.20	
10	Tetracene	-6.60	

Fig. 1. Plot of  $\log(q+1)$  for some polymers against  $pK_b$  for the corresponding molecular compounds analog.

On the other hand, an ion transfer process is expected to respond to the acid-base properties of the polymers. These properties can be compared quantitatively by the  $pK$  ( $-\log[K]$ ) values, where  $K$  is the equilibrium constant for the dissociation reaction of acids and bases. That is, the equilibrium constant for the association and dissociation of a proton.  $pK_b$  values for molecular analogs [20] for 10 of the polymers were found, and these values do have a trend which parallels the  $\log(q+1)$  values in the series. This correlation is shown in Fig. 1. The  $pK_b$  values for the various compounds [20] are listed in the figure. The fit to the line in Fig. 1 is given by  $\log(q+1) = 0.0305pK_b + 0.2731$ , and the quality of the fit,  $R^2$  is 0.91. The  $pK_b$  values reflect the basicity of the model compounds and correspondingly, of the polymer repeat unit, it provides a relative measure of the degree of protonation of the repeat unit. This correlation suggests that the charge observed may be related to the transfer of ions between the contacting surfaces as previously proposed by Diaz et al. [17–19]. In this case, the ions may be protons which result from the dissociation of water molecules on the surface of the contacting surfaces.

A similar trend was found for the donor number (DN) values of the molecular analogs [21], which is the enthalpy associated with the coordination reaction of the repeat unit with metal cations. In this case, values were found for 6 different classes of molecular analogs and the resulting correlation was fit by the equation  $\log(q) = 0.09 \text{ DN} - 0.36$ , and the quality of the fit,  $R^2$  is 0.8. This parallel trend is not surprising since both the  $pK$  and DN parameters are related to the ability of the chemical site to donate a pair of electrons to either a proton center or a metal cation center, respectively.

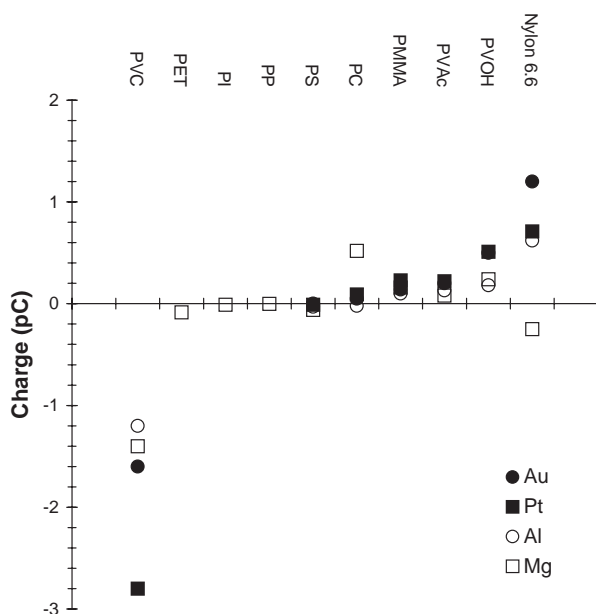


Fig. 2. Semi-quantitative plot of the charge obtained with Au, Pt, Al and Mg.

## 5. Conclusions

The ordering of polymers in four qualitative triboelectric series reported in the literature were compared and found to be similar. A semi-quantitative (Fig. 2) triboelectric series was constructed by combining the individual series and incorporating the quantitative results reported for similar materials in other studies. This now provides a semi-quantitative tribo-charging series containing a wide variety of polymeric materials. This series relates the overlapping results of several reports, and the series can be used to estimate the relative charging capacity of many polymeric materials. The ordering of the polymers in the series parallels the  $pK_b$  and the DN values for the repeat unit analogs of the polymers. This relationship suggests that the charging results are consistent with proton or ion transfer between the surfaces during the contact.

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